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# THE
# KINETIC THEORY OF GASES

## ELEMENTARY TREATISE
## WITH MATHEMATICAL APPENDICES

BY

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*TRANSLATED FROM THE SECOND REVISED EDITION*

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# AUTHOR'S PREFACE

TO

## THIS EDITION

THE first edition of this book appeared in 1877, at the time of the most rapid and beautiful development of the kinetic theory of gases. About twenty years before, the founders of the theory, Krönig and Clausius, had explained the expansive tendency of gases, and had calculated their pressure on the assumption that the smallest particles of gases do not repel each other, but are in rapid motion. From the theory based on this supposition not only were the laws of gases, so far as they were then known, deduced in simplest fashion, but also new laws, hitherto undreamt of, were discovered, which were afterwards confirmed when tested by experiment. These results, which we owe to Maxwell and Clausius, quickly won to the theory many friends and adherents.

But a deeper insight into the new theory was not then widely possessed, since the mathematical shape of the memoirs formed a grave obstacle for many readers. I undertook therefore to exhibit the kinetic theory of gases in such a way as to be more easily intelligible to wider circles, and especially to chemists and other natural philosophers to whom mathematics are not congenial. To this end I endeavoured, much more than was otherwise usual, not only to develop the theory by calculation, but rather to support it by observation and found it on experiment. I therefore collected together, as completely as I could, and summarised, the observations by which the admissibility of the theory might be tested and its correctness proved. I dare to think that I have not failed in this endeavour; for not only did my book receive favourable judgment, but also my presentation of the subject was turned to much account in popular writings and found its way into physical text-books.

In this my book fulfilled the purpose I intended. I wrote it only for that time, and did not seriously think that it might reappear in a new edition after long years. But the demand for the book did not cease, and, as the supply was nearly exhausted more than ten years ago, I had to determine on a revision, although the necessary preliminary work had not yet been done.

As to the general plan of the revision I could not long be in doubt. I could not destroy the shape in which the book had been proved and had won recognition, and I have therefore written it anew on the old plan. The mathematical discussions form, as before, an Appendix which makes no claim to completeness and need not be studied by every reader; the contents of the book are limited to the same range of phenomena as in the first edition; the observations which I have taken into consideration belong partly to mechanical physics and partly to the domains of heat and chemistry. The book has therefore preserved its character, and may perhaps also serve its first purpose.

I have inserted a series of new theories, as, for instance, an explanation on the kinetic theory of the resistance of air and of the reaction of a jet, together with a longer investigation, also new, concerning the influence of the dissociation of the molecules of a vapour upon its viscosity. I should have enlarged the contents of the book in many other directions with pleasure; I should gladly, for instance, have treated of evaporation in connection with the diffusion of gases and have discussed many other subjects allied to the gaseous theory. But I had to omit much, since the work would have demanded too much time. With the present limitation to the old range it has cost very much trouble and very much time to work up the literature of the subject, that has grown mightily in these more than twenty years.

The first German edition of this book has already had a large sale in England and America. The present English translation will contribute to a still wider dissemination of the book, and will win new friends to the kinetic theory. This I confidently hope, now that by reading the proofs I have seen the loving care with which Mr. Baynes has worked at the translation. By numerous suggestions, too, he has enabled me to remove some errors and to make corrections and additions. For this I here express to him my warmest thanks.

OSKAR EMIL MEYER

BRESLAU: *September* 1899

# TRANSLATOR'S PREFACE

HAVING found the first edition of this book of great use, I have willingly undertaken the preparation of an English translation of this greatly enlarged and improved second edition. I have embodied in it all the additional matter contained in the Addenda to the German text, as also certain modifications and additions communicated to me by Professor Meyer, who, by reading the proofs, has ensured their accuracy.

It has been no part of my intention to add any commentary upon the book, but I have appended a few footnotes that seemed advisable, and I have added an Index which I hope will prove useful.

ROBERT E. BAYNES

OXFORD: *October* 1899

## *Addenda and Corrigenda*

P. 46, l. 13: *Add* Planck (*Münchener Sitzungsber.* 1894, xxiv. p. 391; *Wied. Ann.* 1895, lv. p. 220) has attempted to meet Boltzmann's objection (see also *Wied. Ann.* 1894, liii. p. 955) by a change in the form of Kirchhoff's proof, but Boltzmann (*Münch. Sitzungsber.* 1895, xxv. p. 25; *Wied. Ann.* 1895, lv. p. 223) considers that even this amended proof is not perfect. See *Phys. Soc. Abstracts*, 1895, i. pp. 96, 313.

,, 106, 4th formula: *For* $a = a$ *read* $a_p = a$.

,, 139, l. 21: *For* Staigmuller *read* Staigmüller.

,, 232, formula for $\eta$: *Add the exponent* $\frac{2}{3}$ *after* $-$.

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# PART I

# MOLECULAR MOTION AND ITS ENERGY

# CHAPTER I

## *FOUNDATIONS OF THE HYPOTHESIS*

### 1. The Nature of Heat

THE proposition that heat is not a substance, but a form of energy, is no longer considered a hypothesis, but the expression of a certainly proved fact. Experiment shows that heat is generated when mechanical motion is destroyed by friction or otherwise; and, on the other hand, the performance of work by engines that are driven by heat is taken as a proof that heat can be converted into ordinary mechanical energy.

From these and other observations it follows that heat is of the same nature as mechanical work, kinetic energy of visible motion, and all other forms in which energy shows itself in nature. Measurement further proves that the same amount of heat always corresponds to a given expenditure of mechanical energy. Heat therefore undoubtedly forms one of those indestructible magnitudes which we class as energy; or, in other words, heat is energy.

But in every branch of physics generally, as in mechanics, there are two species of energy, which may be distinguished as potential[1] and kinetic,[2] and in heat both species are recognised; latent heat, for instance, is—for the most part at least—potential energy, as it consists of the work spent in overcoming cohesion, while sensible heat, which we feel with our hand and measure with the thermometer, is kinetic energy.

---

[1] The term *potential energy* was applied by Rankine (*Phil. Mag.* [4], v. 1853, p. 106) to the magnitude called *vis mortua* by Leibniz (*Acta Erud.* Lips. 1695, p. 149; collected works, Gerhardt's ed. vi. 1860, p. 238), and later called *Spannkraft* by Helmholtz.

[2] The term *kinetic energy* was first employed by Thomson (Lord Kelvin) and Tait (*Treatise on Natural Philosophy*, Oxford 1867) in place of *actual energy*, Rankine's name for half of the magnitude called *vis viva* by Leibniz. This was termed simply *energy* by Thomas Young (*Lectures on Nat. Phil.* lect. viii. London 1808, p. 79; new ed. 1845, p. 59).

We cannot, therefore, in general use Rumford's[1] expression, and say that heat is motion, but we may assume that *sensible* heat is a mode of motion, though this motion is invisible and almost unknown to us. As its carrier we take the particles, supposed immeasurably small, of which bodies are composed, and to these ultimate particles we ascribe motions of different kinds, assuming that some may move forward in straight lines, that others may oscillate periodically, that others again may revolve about each other —in this small world imitating the planets—and that each may further rotate about an axis of its own; and the sum of the kinetic energies of these motions represents the mechanical energy of the contained heat.

In the mechanical theory of heat we extend this speculation, as a rule, no further, so as not unnecessarily to make our reasonings and conclusions depend on doubtful hypotheses. In this connection physical investigation has special reason to avoid hypothesis, as the high value and great significance of the mechanical theory of heat rest on the general and unconditional validity of its propositions, whereby we are enabled to measure forces of unknown nature equally with known forces, and to subject them to calculation with equal certainty.

It would, however, be a censurable restriction of investigation to follow out only those laws of nature which have a general application and are free from hypothesis; for mathematical physics has won most of its successes in the opposite way, namely, by starting with an unproved and unprovable, but probable, hypothesis, analytically following out its consequences in every direction, and determining its value by comparison of these conclusions with the results of experiment.

For the mechanical theory of heat, too, this method has already borne good fruit. By ascribing special forms to the motion which we call heat—forms which necessarily differ with the nature of the body considered, its state of aggregation and other qualities—we have succeeded in showing that a whole series of important laws of nature necessarily follow from these assumptions, and we may therefore be sure that we have discovered the mechanical cause of these laws in the circumstances of the ultimate particles of bodies. Specially successful have been the labours of those who sought to explain the nature of the gaseous state—doubtless because the heat-motion in gases obeys the simplest laws. From a very simple assumption as to the nature of this motion we have deduced, not only all the laws already known for gaseous bodies, but also new properties which have been most beautifully verified by experiment.

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[1] *Phil. Trans.* lxxxviii. 1798, p. 80.

There has thus arisen from the joint labours of the workers in this field a special theory of the gaseous state which was formerly known as the dynamical,[1] but is now better called the kinetic,[2] theory of gases. In this work I have endeavoured to collect and arrange the scattered contributions of individual authors that have appeared in periodicals of all kinds.

## 2. Hypotheses with regard to Heat-motion

The ultimate elements of bodies whose motion we wish to investigate are not freely movable each by itself; they are bound together by mutual forces—their affinity, whence arise combinations of atoms into larger masses called molecules.

We may therefore distinguish two kinds of heat-motion, atomic and molecular. By the latter we understand the translatory motion of the centroid of the atoms that form the molecule, while as atomic motion we count all the motions which the atoms can individually execute without breaking up the molecule. Atomic motion includes, therefore, not only the oscillations that take place within the molecule, but also the rotation of the atoms about the centroid of the molecule.

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[1] Maxwell, *Phil. Mag.* [4] xix. 1860, p. 19, xx. 1860, p. 21.

[2] So far as I know, this name was first used by Lord Kelvin (Sir W. Thomson) in an address before the British Association at Edinburgh (*B.A. Rep.* 1871, p. 93); Maxwell afterwards adopted it (*Nature*, viii. 1873, p. 298; *Scientific Papers*, ii. p. 343).

This division of the whole heat-motion corresponds to the division of physical science into physics and chemistry —not, indeed, in every respect, but in so far as chemistry deals chiefly with the equilibrium of atoms, while physics treats more of the mechanics of molecules.

Chemical equilibrium, or the unchanged existence of molecules, is attained when the affinity which holds the atoms together is in equilibrium with the forces that tend to break up the molecule; such forces arise from the motion of the atoms, partly from the collisions of those which vibrate, and partly from the centrifugal tendency of those which rotate. Since then, in a chemically stable body, the atomic motions are kept in continuous dynamical equilibrium with the chemical forces, and their action is overcome by the latter, only the molecular motion comes primarily into account in the investigation of purely physical forces and phenomena, and we therefore limit the range of our discussion in the first place to the latter.

Just as the atomic motion tends to break up a molecule, so the molecular motion tends to loosen the connection between the parts of a body, partly in consequence of collisions between the molecules, and partly from their centrifugal tendency; and equilibrium is maintained—at least when there is no external pressure—by cohesion, a force in which we need see nothing different from affinity. It seems enough to account for cohesion in an excess of affinity over the dissociating action of atomic motion, which is not large enough to attract an atom into the pale of a molecule and to keep it there, but is sufficient to bind together neighbouring molecules in a much less close bond.

The problem of discovering the laws of molecular motion is therefore identical with that of determining the laws of cohesion, since when the medium is in equilibrium the forces due to this motion are equilibrated by those of cohesion.

The difficulty of this problem disappears in the special case which is the subject of this work.

## 3. Behaviour of Gases

In gaseous bodies scarcely a trace of cohesion can be found. In these most attenuated of all known media the molecules seem so far apart that one experiences no attraction by another, except in the rarely occurring case of two molecules coming accidentally very close, or even into collision, in consequence of their motion.

This theoretical view explains in the simplest manner the tendency of gases to expand, and it has a further support, derived from experiment, in the thermal behaviour of gases when changing volume. For if a gas expands without overcoming pressure, and therefore doing work—if, for instance, it streams into vacuous space—its temperature falls so little that for long it was admitted, on the evidence of Gay-Lussac's experiments, that under such circumstances no fall of temperature at all occurs.

This behaviour would not be possible if on expansion a gas had to overcome any considerable cohesion, since for this an expenditure of energy, and therefore of heat, would be requisite. Just as little can the assumption of repulsive forces between the molecules be reconciled with this experiment, since such forces would come into play during expansion and generate energy in the shape of an increase of heat in the gas.

By the more exact experiments made by Joule and Lord Kelvin on the heat-effects of gases in motion, it is, indeed, shown that there is cohesion between the particles even of gases; but the above conclusions are not thereby invalidated, since Joule and Lord Kelvin's values for the work done by an expanding gas in overcoming its own cohesion are of nearly vanishing magnitude.

It is specially important for our theory to note that all experiments that have been made to determine this small amount of work agree in showing a real cohesion in so far as it was proved that particles of gas attract, and do not repel, each other. Herein is a weighty support of our hypothesis, since in face of this fact the possibility of explaining, as Newton attempted, the expansive tendency of a gas by the repulsion of its particles disappears; and there remains as the only admissible hypothesis the opposite view that in a motion of its molecules consists the expansive tendency of a gas.

## 4. Character of the Heat-motion in Gases

It is now easy to determine the way in which we have to represent to ourselves this molecular motion. We first assume that the gas under consideration is removed from the action of external forces—such as gravity, for instance—and we then introduce the further assumption, which is sufficiently, though not strictly, accurate, that there is no cohesion in the gas worthy of account.

If these two suppositions are realised the molecules of a gaseous substance move freely without being subject to the action of any force. Now, according to the law of inertia, free motion without the action of force takes place with unchanging speed in unchanging direction. Hence the hypothesis which must form the groundwork of the theory of gases is this:—

*The heat-motion of the molecules of a gas consists in a uniform rectilinear translatory motion.*

We must add to this what is nearly obvious, namely, that a molecule can proceed along its straight path only so long as it meets with no obstruction. If it should strike a wall or collide with another molecule, its motion must suffer an abrupt change in direction by reason of the impenetrability of matter. Two colliding molecules therefore rebound from each other, and possibly just like two elastic balls.

If, now, we take account of the action of external forces, such as gravity, which is practically uniform, we have to represent the paths of the molecules as no longer straight, but in general curved, the path for a constant force being a parabola. This curvature of the path under the action of gravity will, however, be quite insignificant if the speed of the molecules is very great. Since this condition is actually fulfilled, as the numbers in § 13 show, we may neglect this curvature and consider the molecular motions in even heavy gases as rectilinear.

Of more importance is the fact that gases are not quite free from cohesion of their particles, but exhibit distinct, though very slight, traces of it. Two gaseous molecules, however, can only attract each other when sufficiently near, so that if a gas is not too strongly compressed, but is far from the point of liquefaction, we are justified in representing an overpowering majority of its molecules as far enough apart to be nearly always outside the range of their mutual attraction; and we may therefore assume that the small amount of cohesion which does come into play is to be put to the account of the rarely occurring cases when two molecules now and then come very near each other.

If we therefore represent the molecules of a gas as moving in general in a straight line, and only changing direction when two approach very closely, this view is practically the same as that enunciated for the simple case first given, the difference between them consisting only in the substitution of a rapid, though gradual and continuous, change of direction in the motion of two molecules on very close approach to each other, in place of a sudden rebound on collision.

The most essential point of our hypothesis is not thereby touched; it remains true that a gaseous molecule moves *with uniform velocity in a straight line* between every two successive collisions with other molecules.

## 5. Founders of the Kinetic Theory

When these views on the nature of the gaseous state were published in 1856 by Krönig,[1] and in 1857 by Clausius,[2] they aroused very special remark by their novelty and their entire variation from the ideas till then current. The mathematical theory which Clausius founded on this hypothesis, and published in the memoir cited, as well as in later papers, especially attracted attention, and many physicists were induced by these investigations to help in developing the theory and putting it to experimental proof.

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[1] *Grundzüge einer Theorie der Gase:* first published separately in Berlin by A. W. Hayn, and then in *Pogg. Ann.* xcix. 1856, p. 315.

[2] *Ueber die Art der Bewegung, welche wir Wärme nennen, Pogg. Ann.* c.

It was, indeed, quickly found that these views on the nature of gases were not new, but had been published very often before Clausius, and indeed with perfect clearness very long before. Clausius himself mentioned in his first memoir a paper published by Joule[1] in 1851, which had remained almost quite unnoticed, wherein the question is taken up and treated in essentially the same way; and Joule refers to a paper by Herapath[2] which appeared in 1821. In 1845 there was also presented to the Royal Society of London a paper by Waterston,[3] which proceeds on the same lines regarding molecular motion, but, for certain faults, was not printed till Lord Rayleigh published it on account of its historical interest.

A whole series of writers have further been named who are said to have held and published similar views and to have expressed them with more or less clearness; this list, beginning with the philosophers of classical antiquity, runs through the Middle Ages to the last century. Of all these writers, however, there is but a single one of consequence from the present state of the theory, viz. Daniel Bernoulli,[4] whose memory Franz Neumann has preserved for his pupils and posterity, and to whom P. du Bois-Reymond[5] has directed the attention of his contemporaries by a German translation of a fragment of his

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1857, p. 353; *Abhandlungen über die mechanische Wärmetheorie*, Brunswick 1867, 2nd part, p. 229; transl. *Phil. Mag.* [4] xiv. 1857, p. 108.

[1] *Memoirs of the Manchester Lit. and Phil. Soc.* [2] ix. 1851, p. 107; reprinted later *Phil. Mag.* [4] xiv. 1857, p. 211.

[2] *Annals of Philosophy* [2] i. 1821, pp. 273, 340, 401.

[3] *Phil. Trans.* clxxxiii. 1892, p. 1.

[4] *Hydrodynamica*, Argentorati 1738, Sect. X. D. & J. Bernoulli, *Nouv. Princ. de Méc. et de Phys. &c.* Rec. des pièces de prix, v. 1752.

[5] *Pogg. Ann.* cvii. 1859, p. 490.

works. The writings of the others have now only a historic interest,[1] as they exhibit, in the rise and fall of a philosophical system, a picture of the intellectual life of man which becomes the more distinct by a narrow limitation to a special study.[2] The kinetic theory of our day has come to life quite independently of those forgotten predecessors. We may look on Daniel Bernoulli as the first author of the fundamental notion of the kinetic theory—so at least I think I have proved in the following pages; but he who has the honour of being acknowledged as the author of a scientific system—a mathematical theory—founded on this notion is Clausius, and with him Maxwell has done the most to promote and develop the theory.

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[1] Gehler's *Physik. Wörterbuch*, iv. 1828, p. 1049; Clausius, *Pogg. Ann.* cxv. 1862, p. 2, *Abhandl.* pt. ii. p. 230; transl. *Phil. Mag.* [4] xxiii. 1862, pp. 417, 512; Lothar Meyer, *Theorien der Chemie*, 2nd ed. p. 29, 5th ed. p. 30.

[2] A thorough exposition of the 'Fall of the kinetic theory of atoms in the seventeenth century' is given by Dr. Kurd Lasswitz in *Pogg. Ann.* cliii. 1874, p. 373, as well as in his *Geschichte der Atomistik*, 2 vols., Hamburg and Leipsig 1890. The influence of the corpuscular philosophy is there portrayed, and the harm done by Newton's doctrine of the kinetic theory of atoms. I might add that it fell into complete oblivion in the eighteenth century, when the Cartesian philosophy, with which it was in constant strife, was supplanted and Kant's arose; and it remained forgotten by all, with few exceptions, of the natural philosophers of the present century, who take but little account of older works.

# CHAPTER II

## *PRESSURE OF GASES*

### 6. Boyle's Law

THE hypothesis, which we have described, of the to-and-fro motion of the molecules of a gas in straight paths, of their collisions and subsequent separations, and of their striking against the walls of the containing vessel, furnishes a very simple explanation of the cause of the pressure which the gas exerts. This pressure results from the series of impacts of the molecules, as they move to and fro, against the enclosure. As the first test of the admissibility of our hypothesis, we have to see whether this explanation of the pressure is in agreement or not with the laws of gaseous pressure that have been deduced from experiment.

The law with which we have first to deal is in Germany generally called Mariotte's law, because Mariotte enunciated it at the head of his essay 'De la Nature de l'Air,' which first appeared in 1679. As, however, there can be no doubt that the discoverer[1] of this law is Robert Boyle,[2] who determined it seventeen years earlier, I shall follow the English custom of calling it Boyle's law.

That this law—viz. that the density and pressure of a gas are proportional to each other—is not in contradiction with the kinetic theory, but, on the contrary, is a necessary result of the hypothesis of rectilinear motion, was proved by Daniel Bernoulli,[3] the originator of this hypothesis.

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[1] See, for instance, Muncke in Gehler's *Physikal. Wörterbuch*, 1828, iv. pp. 1026, 1028.

[2] 'A Defence of the Doctrine touching the Spring and Weight of the Air,' London 1662, Pt. II. Chap. V.

[3] *Hydrodynamica*, Argentorati 1738, Sect. X. p. 200; reprinted in German, *Pogg. Ann.* cvii. 1859, p. 490.

Bernoulli supposed a mass of gas to be confined in a vessel with a movable but air-tight lid, such as the cylinder of an air-pump; this gas can be compressed by increasing the pressure on the lid or piston. If, now, the gas consists of a large number of moving particles, and the pressure exerted by it on the walls of the vessel arises from the impacts of the particles against these walls, then equilibrium results when the resultant action of the impacts on the lid is equal to the pressure applied to it.

If the gas is compressed and the volume diminished, the number of impacts of the now more closely packed particles against the walls increases, and for two reasons: first, there is a larger number of particles in the layer of gas immediately adjoining the walls; and, secondly, as the particles are more crowded together, they collide oftener, and, hurled back by the collision, are oftener flung against the walls. If, by the compression of the gas, the volume is diminished in the ratio $1 : s^3$, the distance between any pair of particles is diminished in the ratio $1 : s$; the number of particles, therefore, in the bounding layer, which is in contact with a given area of the walls, is increased in the ratio $s^2 : 1$; further, the number of collisions that take place between the molecules in a given time is increased in the ratio $s : 1$; and in this same ratio also is the number of impacts of any particle in the bounding layer against the walls increased. Since, then, the number of impinging particles is increased in the ratio $s^2 : 1$, and the number of impacts by each in the ratio $s : 1$, the number of impacts against a given part of the walls in a given time is increased in the ratio $s^3 : 1$, which is the inverse of the ratio in which the volume of the gas is diminished. *The pressure*, therefore, *of a gas varies inversely as its volume.*

$\frac{\Delta v}{v} = \frac{1}{s^3}$

$\frac{\Delta l}{l} = \frac{1}{s}$

Boyle's law is thus deduced from the hypothesis of molecular impacts.

## 7. The Admissibility of the Hypothesis

Since Boyle's law can be deduced also from quite different assumptions, this first consequence of the theory is no proof of the exclusive claims of our kinetic hypothesis; but it allows us to judge for what substances, and under what circumstances, the theory may be considered admissible.

Boyle's law is not obeyed by all substances in the gaseous state. The vapours of liquid bodies do not obey it except within certain limits of pressure and temperature, and then only with moderate approximation. Even the so-called permanent gases do not satisfy the law rigorously and under all circumstances.

This was known to Boyle himself, and the inexactness of the law has been confirmed by Musschenbroek and a whole series of physicists, ancient and modern, such as Despretz, Arago and Dulong, Pouillet, Regnault, Siljeström, Mendelejeff and Kirpitscheff, Amagat, Cailletet.

It would be out of place here to enter fully into the results of the numerous investigations undertaken to test Boyle's law, as this work does not profess to be a complete text-book of the physics of gases, and the more detailed text-books[1] contain full information. A few examples are here sufficient, which show how far the real gases depart from Boyle's law under ordinary circumstances, that is, at mean temperatures and under moderate pressures.

If this law were strictly exact, the product of the pressure $p$ into the volume $v$ of a mass of gas would be a magnitude which would not alter in value when the pressure took the value $P$ and the volume the corresponding value $V$; we should, therefore, have

$$\frac{pv}{PV}=1,$$

if, as we assume, the temperature did not alter. The following table contains for a series of gases the values of this ratio which Regnault[2] found on increasing the pressure from $p=1$ atmosphere to $P=2$ atmospheres.

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[1] Winkelmann, *Handbuch der Physik*, i. p. 503; Ostwald, *Allgemeine Chemie*, 2nd ed. i. p. 139; &c.

[2] *Mém. de l'Acad. de Paris*, xxi. 1847, p. 329; xxvi. 1862, p. 260.

| Gas | | $\frac{pv}{PV}$ | Gas | | $\frac{pv}{PV}$ |
|---|---|---|---|---|---|
| Hydrogen | $H_2$ | 0·999 | Carbon dioxide | $CO_2$ | 1·008 |
| Nitrogen | $N_2$ | 1·001 | Hydrogen chloride | HCl | 1·009 |
| Oxygen | $O_2$ | 1·002 | Hydrogen sulphide | $H_2S$ | 1·011 |
| Nitric oxide | NO | 1·003 | Ammonia | $NH_3$ | 1·019 |
| Carbon monoxide | CO | 1·003 | Sulphur dioxide | $SO_2$ | 1·021 |
| Marsh gas | $CH_4$ | 1·006 | Cyanogen | CN | 1·024 |
| Nitrous oxide | $N_2O$ | 1·007 | | | |

This table shows that Boyle's law does not hold exactly for any gas, but that for the gases named it holds with sufficient approximation to be considered for most purposes an exact law of nature. The vapours of liquids, indeed, depart from the law more widely than gases; but from a theoretical calculation to which Clausius[1] has subjected Regnault's observations on saturated steam, it appears that for this vapour from 0° to 100° the values of the magnitudes, which according to the law should be constant, vary by not more than 5 per cent. at the most. Similar relations were found by Herwig[2] for the unsaturated vapours of alcohol, chloroform, and carbon disulphide.

Accordingly, therefore, the departures of even the vapours of liquid bodies from the law inferred from theory are sufficiently unimportant to be provisionally neglected when we attempt to investigate the other properties of these bodies on the basis of this theory. Strictly speaking, our further conclusions will only be rigorously true for such media as obey Boyle's law exactly; these, however, exist only in the imagination, and are therefore called *ideal* (or *perfect*) *gases.* But, in the main, our considerations are also true for real gases, and the variations between the theory and observation will be of no greater importance than that of the differences in the foregoing numbers.

## 8. Defects of the Hypothesis

We shall, however, not rest content with this approximation, but try to get nearer the truth by inquiring into the possible causes of these variations. If Bernoulli's theory gives, as its necessary consequence, a law that is only approximately exact, the hypothesis underlying the theory cannot be quite true in every respect, but must be defective, even if only slightly.

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[1] *Pogg. Ann.* lxxix. 1850, p. 513, Clausius, *Mechanische Wärmetheorie,* 2nd and 3rd ed: i. p. 151; transl. *Phil. Mag.* [4] ii. 1851, p. 102.

[2] *Pogg. Ann.* cxxxvii. 1869, pp. 19, 592.

In the assumptions with which we started there are two different points which cannot be directly proved, and are therefore open to doubt. The first is the assumption that gases are made up of molecules of very small dimensions, and the second is the assumption that in gases there is no cohesion. Neither of these is exactly true, and therefore neither can be admitted except as an approximation to the truth; and in their inexactness lies ample ground for the departures from Boyle's law.

In the first place, if the dimensions of the molecules are not indefinitely small, the calculation which led to the law is not exact. For it is only if the space actually occupied by the molecules is absolutely negligible in respect of the volume which contains them that we may justifiably conclude that the frequency of collision is increased in the ratio $s : 1$ by a diminution of the volume in the ratio $1 : s^3$. If this condition is not fulfilled there is less actual distance between the molecules, which, therefore, collide the oftener with each other and in the same ratio impinge the oftener against the walls of the vessel—in other words, the pressure is greater than according to the former calculation; and as this increment in the pressure is the more considerable the less the volume, the pressure must increase at a greater rate than the volume diminishes. The denominator $PV$ of the ratio considered in § 7, wherein $P$ denotes the higher pressure, is on this account greater than the numerator $pv$, so that the ratio $pv/PV$ has, as actually happens with hydrogen, a value less than 1.

A deviation in the reverse direction occurs when the second hypothesis is sensibly in fault and the gas has marked cohesion. For such a property will tend to lessen the volume, which will, therefore, on this ground diminish more rapidly than the pressure increases; $PV$ will thus be smaller than $pv$ and the ratio $pv/PV$ greater than 1, as is the case with all the gases in the table of § 7, except hydrogen.

Probably both influences occur in nature, and the numbers in Regnault's table seem to show that in the case of most gases the influence of cohesion is predominant so long as the pressure lies within certain limits. But when higher pressures are employed all gases exhibit, according to the observations of Natterer,[1] Amagat,[2] and Cailletet,[3] the same behaviour as under lower pressure is noted with hydrogen. The product $PV$ increases with the pressure $P$, because on account of the dimensions of the molecules the volume $V$ cannot diminish so much as the law requires.

These considerations, which we shall repeatedly have again to take up and extend,[4] show that the departures from the strict law can also be explained by the theory. Since the probability of the theory is, therefore, in no respect prejudiced by the inexactness of Boyle's law, we are entitled to draw further inferences and conclusions, first of all, from the simple theory, and to reserve their correction for later chapters.

## 9. Increase of Pressure by Heat

Bernoulli also saw that his theory accounted not only for Boyle's law, but also for the observed increase in the pressure of a gas to which heat is communicated. According to the laws of thermodynamics heat is energy; an increase of heat, therefore, consists in an augmentation of the speed of the molecular motion, and this increase of speed entails increase both in the number of impacts of the molecules of the gas against the vessel and also in the strength of these impacts. For a double reason, therefore, the resultant action of the impacts in a given time, *i.e.* the pressure of the gas, is increased by an addition of heat.

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[1] *Pogg. Ann.* lxii. 1844, p. 132, xciv. 1855, p. 436.

[2] *Comptes Rendus*, lxxxviii. 1879, p. 336; *Ann. Chim.* [5] xix. 1880, p. 345, [6] xxix. 1893, p. 68.

[3] *C. R.* lxx. 1870, p. 1131, lxxxviii. 1879, p. 61; *Journ. de Phys.* viii. 1879, p. 267.

[4] See Chap. IV. §§ 40–51.

Beyond these considerations no further proof is needed of the proposition that the pressure increases as the square of the molecular speed, or, what comes to the same thing, as the energy of the molecular motion. In agreement, therefore, with the general principles of thermodynamics it follows that *the mechanical measure of heat and of temperature is the kinetic energy of the molecular motion.*

## 10. Mean Value and Components of the Energy

The closer investigation of the relation between the temperature of a gas and the kinetic energy of its molecules is rendered difficult by the circumstance that the molecules have not all the same speed, and, therefore, not all the same energy. This consideration is really identical with this other, that the energy of each particle changes on collision. If, however, we can say that the resultant action of the impacts which each particular molecule makes in a fairly long time with its energy ever changing is equal to that which would result if the impacts all occurred with a uniform mean energy, then we must allow that the resultant action of the impacts of all the molecules is the same as if the molecules have all a uniform mean energy of motion.

We gain a further advantage in our calculation by making use of the proposition that, just like a velocity or a force, kinetic energy may be separated into three components, of which each corresponds to a component of the motion in a given direction. The whole energy is equal to the sum of its components, as is easily seen from the known formula

$$\omega = \sqrt{(u^2 + v^2 + w^2)}$$

for a velocity $\omega$ in terms of its rectangular components $u, v, w$; for this gives

$$\tfrac{1}{2}m\omega^2 = \tfrac{1}{2}mu^2 + \tfrac{1}{2}mv^2 + \tfrac{1}{2}mw^2.$$

This proposition enables us to substitute a simpler motion for that which really goes on in the gas near the walls of the vessel and produces pressure on it: we divide the kinetic energy of all the molecules into three parts which in the mean are all of equal magnitude, one of them being the energy of a motion at right angles to the wall, and the others corresponding to motions which are parallel to the wall and at right angles to each other.

Only the first of these components of the energy comes into account in the estimation of the pressure on the vessel, and we therefore find the correct value of the pressure by ascribing to all the molecules a velocity perpendicular to the wall and a kinetic energy equal to one-third of the total mean kinetic energy of a molecule.

This result of our investigation is identical with the assumption with which Joule[1] and Krönig[2] started in their calculations, as they assumed a gas, enclosed in a cube, to press as strongly against the faces as if one-third of the molecules moved parallel to each of the three directions of the edges, so that each face was impinged upon by only one-third of all the molecules.

## 11. Calculation of the Pressure[3]

With this simplified assumption it is easy to calculate the value of the pressure from the resultant action of the impacts which the surface undergoing pressure receives from the molecules that meet it.

This surface, which we will call the *stressed surface*, may be taken either as a mathematical plane or surface inside the space filled with gas, or as a wall of the containing vessel. The former assumption has the advantage of allowing the calculation to proceed without further hypothesis being necessary; here, however, I will first investigate the value of the pressure exerted on a solid wall by reason of its greater intelligibility.

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[1] *Mem. of the Manchester Lit. and Phil. Soc.* [2] ix. 1851, p. 107; *Phil. Mag.* [4] xiv. 1857, p. 211.

[2] Berlin 1856; afterwards reprinted in *Pogg. Ann.* xcix. 1856, p. 315, and in many other periodicals.

[3] Other calculations beside those of Joule and Krönig: Clausius, *Pogg. Ann.* c. 1857, p. 353; Maxwell, *Phil. Mag.* [4] xix. 1860, p. 29, xxxv. 1868, p. 195; Stefan, *Wiener Sitzungsberichte*, xlvii. 1863, p. 91; O. E. Meyer, *De Gasorum Theoria*, Vratisl. 1866; Pfaundler, *Wien. Sitzungsber.* lxiii. 1871, p. 159; v. Lang, *ibid.* lxiv. 1871, p. 485, *Pogg. Ann.* cxlv. 1872, p. 290; Saalschütz, *Schr. d. phys.-ökon. Ges. zu Königsberg*, 19. Jahrg. 1878, *Sitzungsber.* p. 45.

For this it is necessary to introduce a hypothesis as to the magnitude of the forces exerted by impact against the wall. In choosing this we shall have to be guided by the consideration that a gas suffers no loss of energy through exerting pressure on the solid walls of its enclosure; the gas therefore receives back from the wall the energy it has given to it. If this is true for the gas as a whole we shall have also to assume for each one of its molecules that at every single impact against the wall its stock of kinetic energy remains undiminished. We thus arrive at the hypothesis that each molecule is, like a perfectly elastic ball, thrown back from the wall with the same speed with which it struck it. A molecule that impinges perpendicularly against the wall receives an impulse which is sufficient not only to stop its motion, but also to give it an equal speed in the reverse direction. The magnitude of this impulse is expressed by the product $2mG$, wherein $m$ denotes the mass of a molecule and $G$ its speed; and just as great is the impulse exerted on the wall by the molecule during the impact.

To obtain from this the total force exerted on the wall we have to multiply this expression by the number of impacts in the unit of time.

Although this calculation can be made for every possible shape of the enclosure containing the gas, we will for simplicity consider the gas to be in a rectangular parallelopiped, whose edges are $\alpha, \beta, \gamma$ in length, so that its volume is $\alpha\beta\gamma$. If now there are $N$ molecules per unit volume, there are $N\alpha\beta\gamma$ molecules altogether. According to Joule's representation of the case, which, as was proved in § 10, may be used in the calculation instead of the real circumstances, one-third part of this number, or $\frac{1}{3}N\alpha\beta\gamma$ molecules, move in the direction of the edge $\gamma$ perpendicularly against the two faces $\alpha\beta$. These faces will be struck alternately by the molecules moving to and fro between them.

The number of impacts on one of these faces in the time-unit is found from the consideration that between every two successive impacts by one and the same molecule there elapses the interval during which the molecule passes to and fro between the faces, that is, the interval in which it traverses the path $2\gamma$ with the speed $G$. The number of impacts, therefore, which a single particle makes on the face in a unit of time is the ratio of the path $G$ traversed in the time-unit to the length $2\gamma$ of the path to and fro, and is thus $G/2\gamma$; hence the number of impacts on a face $\alpha\beta$ in the unit of time made by all the particles is

$$\tfrac{1}{3}N\alpha\beta\gamma \times G/2\gamma = \tfrac{1}{6}NG\alpha\beta.$$

The product of this number into the impulse $2mG$, which is in the mean exerted at each impact, gives for the whole impulse exerted on the face $\alpha\beta$ in the unit of time, that is, for the total force exerted on it,

$$p\alpha\beta = \tfrac{1}{3}NmG^2\alpha\beta,$$

$p$ being the pressure; so that the pressure on the surface is given by

$$p = \tfrac{1}{3}NmG^2.$$

This formula confirms what has been deduced before, viz. that the pressure $p$ is directly proportional both to the square of the speed (§ 9) and also to $N$, the number of molecules in unit of volume, and therefore to the density of the gas; it is consequently inversely proportional to the volume (§ 6).

## 12. Another Calculation of the Pressure

I do not wish, however, to be content with this one calculation of the pressure, as it suffers from the defect of containing an unproved and unprovable hypothesis which it would have been easy to avoid—I mean the hypothesis that the laws of elastic impact hold for the collisions of molecules, even if only to a limited extent. We do not need this hypothesis if we investigate the pressure in the interior of the gas in place of that on the walls; and this interior pressure can be calculated by the following method, which is carried out with greater strictness and generality in the Mathematical Appendix No. 1, §§ 1*–7*.

Consider the space occupied by the gas to be divided by a plane into two halves, a right half and a left half, and mark off a bit of this plane of unit area. On this unit area the one half of the gas presses with the same intensity from its side as the other half from the opposite side. For the right half would be moved from left to right by the pressure exerted on it by the left half, if it did not itself exert an equal and opposite pressure. Now, we measure a continuous force by its impulse in a unit of time; in the meaning of our theory, therefore, the pressure is nothing else than the momentum which is transferred in unit of time through the unit area of the plane from one half of the gas to the other, or, rather, as need hardly be specially specified, it is the component of this momentum in the direction of the pressure. To find the value of the pressure we have therefore to calculate the momentum perpendicular to the unit area which is transferred from one half of the gas to the other by the molecules that cross the unit area in a unit of time.

If for simplicity we retain Joule's conception of breaking up the motion into three components, we have to assume that one-third of all the molecules move perpendicularly to the plane. One-half then of this one-third—*i.e.* one-sixth of the whole—move at any moment from left to right, while an equal number move from right to left.

In a unit of time those molecules only can cross the plane whose distances from it at the beginning of the time-unit are less than the length of path travelled during the time-unit. Hence all the molecules which cross the unit area from left to right in a time-unit come from the cylinder, whose base is the unit area, and whose height is measured by the speed $G$, and whose volume therefore is numerically equal to $G$. The number of molecules therefore which cross unit area of the plane in unit time from the left half of the gas to the right is $\frac{1}{6}NG$, if $N$, as before, represents the number of molecules in the unit of volume.

Since each of these molecules, being of mass $m$ and moving with speed $G$ from left to right, carries over into the right half the momentum $mG$, the molecular momentum of this half from left to right will have been increased by the passage of molecules over this unit area in the unit of time by the amount

$$\tfrac{1}{6}NG \times mG = \tfrac{1}{6}NmG^2\,;$$

while simultaneously the same number of molecules cross the area from right to left, diminishing thereby the oppositely directed—from right to left—momentum of the right half by the same amount; and therefore there is produced in the right half an excess of the left-to-right molecular momentum over that from right to left of twice this amount, or of $\tfrac{1}{3}NmG^2$. This excess acts continuously during the given time—viz. the time-unit—as a force from left to right on the right half of the medium, and it is nothing else than the pressure

$$p = \tfrac{1}{3}NmG^2,$$

which is balanced by the oppositely directed pressure of the other half.

This formula is the same as that found before, and thus proves that its validity is not bound up with the assumption before made, which assimilated the problem to that of elastic collision.

## 13. Absolute Value of the Molecular Speed

The product $Nm$ in the last formula, of the mass of a molecule $m$ into the number $N$ of the molecules contained in unit volume, has a simple meaning, for it obviously represents the mass of gas in the unit of volume; but this may be shortly called the *density* of the gas, the density of water—of which the mass-unit, one kilogram, occupies the volume-unit, one litre—being the unit density. This definition of the density $\rho$ gives

$$Nm = \rho.$$

Consequently the formula may be written

$$p = \tfrac{1}{3}\rho G^2,$$

in which form its agreement with Boyle's law, viz. that the pressure of a gas is proportional to its density, is more directly seen.

In this new form, however, it teaches us much more; it empowers us to draw a remarkable and very important conclusion. Since two of the magnitudes occurring in the formula, viz. the pressure $p$ and the density $\rho$, are directly amenable to observation and measurement, the formula allows us to deduce from them the third, viz. the value of $G$, the mean speed of the molecules, *in absolute measure*. It was Joule[1] who by this conception opened up to investigation a field which one would have been tempted to think was closed to human knowledge; and Clausius[2] followed him along the path thus trodden to explore an unseen world.

Though measured by the height $h$ of a column of mercury, the pressure $p$ is not identical with this height, but with the action of gravity on the column when taken of unit area. If, then, $q$ denotes the density of mercury and $g$ the acceleration of gravity, we have

$$p = gqh,$$

and therefore $G$ is given by

$$G^2 = 3gqh/\rho.$$

Let us make this calculation for the temperature 0° C. and the pressure of one atmosphere, *i.e.* of a column of mercury 0·76 metre high. We will take Regnault's[3] value, $q = 13{\cdot}596$, and his values for the density of the various gases; we must therefore take the value of gravity for Paris, where Regnault made his observations, and put $g = 9{\cdot}80896$ metres per sec. per sec. The density $\rho$ of the gas is, like the density $q$ of mercury, to be referred to water as unity; but if instead it is referred to air, which under the given circumstances is 773·3 times lighter than water at 4° C.,[1] we must put

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[1] *Mem. of the Manch. Lit. and Phil. Soc.* [2] ix. 1851, p. 107; *Phil. Mag.* [4] xiv. 1857, p. 211.

[2] *Pogg. Ann.* c. 1857, p. 375; *Abhandl. über d. Wärmetheorie*, pt. ii. 1867, p. 254; transl. *Phil. Mag.* [4] xiv. 1857, p. 108.

[3] *Mém. de l'Acad. de Paris*, xxi. 1847, p. 162.

$$\rho = s/773{\cdot}3,$$

where $s$ is the specific gravity of the gas. We obtain in this manner, according to Clausius's calculation, a general formula for the value of the mean molecular speed of a gas at 0° C., which we will denote by $\mathfrak{G}$, viz.

$$\mathfrak{G} = 485/\sqrt{s} \text{ metres per second,}^2$$

which holds good for all pressures and places, though the special circumstances of Regnault's observations were employed in its calculation.

From this formula Clausius[3] has deduced the following values for the mean molecular speeds of atmospheric air and other gases at 0° C. in metres per second:

| | *Values of* $\mathfrak{G}$ |
|---|---|
| Air | 485 |
| Oxygen | 461 |
| Nitrogen | 492 |
| Hydrogen | 1844 |

The surprising magnitude of these numbers may serve as new evidence of the degree in which heat, the cause of these rapid motions, is superior to the mechanical forces which are at our disposal in capability for doing work; and they further justify the assertion in § 4, which is there not proved, that the speeds produced by gravity in short periods are too small in comparison with these speeds to cause any sensible parabolic curvature in the paths of the molecules.

But, on the other hand, these molecular speeds are not so great that in comparison with them gravity can be absolutely neglected. If this were so, the continuance of an atmosphere about the earth would be impossible, as all the molecules of the air would disperse into space in consequence of their speed.

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[1] Regnault found $\rho = 0{\cdot}00129321 = 1/773{\cdot}270$, and Broch (*Trav. et Mém. du Bureau Int. des Poids et Mes.* 1881, pt. i. p. 49) $\rho = 0{\cdot}00129305 = 1/773{\cdot}365$.

[2] [Regnault's value of $\rho$ gives 484·898, and Broch's 484·928, and the number 773·3 for the value of $s/\rho$ gives 484·907.—Tr.]

[3] *Pogg. Ann.* c. 1857, p. 377; *Abh. ü. Wärmetheorie*, pt. ii. 1867, p. 256; *Mechanische Wärmetheorie*, 1889–91, 2nd ed. iii. p. 35, edited by Planck and Pulfrich.

A body thrown vertically upward with a speed of 485 metres per second would rise to a height of 12,000 metres and then fall back again. A molecule of air, therefore, which moves at the earth's surface with a calculated mean speed of 485 metres per second, cannot in consequence of this rise higher than 12,000 metres, and remains, therefore, within the much higher atmosphere. Just as little can molecules in higher layers leave the atmosphere, as these layers are colder, and the molecular speed is therefore smaller.

To entirely escape from the earth without returning, a molecule of air must have at the earth's surface a speed of at least 11,000 metres per second, which is twenty times larger than the mean speed at 0°; but we are in a position [1] to assume that such a speed can never occur—or, at most, only very exceptionally.

On the moon, whose diameter is four times less than that of the earth, the acceleration of gravity is nearly six times less than on the earth; consequently a molecule of air with the speed 485 metres per second could rise to a height of 74 kilometres, and to escape entirely from the moon it would require a speed of only 2,400 metres per second. From this we may conclude that if the moon possesses an atmosphere at its general low temperature it can in any case have only a very thin one.[2]

## 14. Temperature

The values found for the mean molecular speed are those at 0° C., and it has already been pointed out in § 9 that this speed increases with the temperature. To determine in what ratio this increase takes place we have to compare the formula which theoretically expresses the pressure with the laws regarding the pressure that have been deduced from experiment. This comparison leads to a definition of the nature of temperature in reference to the conceptions underlying our theory.

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[1] Compare §§ 24, 26, 28.

[2] Bull, Liveing, and Bryan, *Meteorologische Zeitschrift*, xi. 1894, p. 76. G. Johnstone Stoney, *Astrophys. Journ.* 1898, vii. p. 25; *Journ. de Phys.* [3] vii. p. 528.

The empirical law, discovered nearly simultaneously by Gay-Lussac[1] and Dalton,[2] which expresses the dependence of the pressure of a gas on its temperature, is contained in this amended form of Boyle's law, viz.:

$$p = k\rho(1 + a\vartheta),$$

where $p$ and $\rho$ denote the pressure and density as before, $\vartheta$ is the temperature C., $k$ a constant, and $a$ the thermal coefficient of expansion, or, more correctly, the coefficient of increase of pressure.[3]

From this and the formula proved before, viz.

$$p = \tfrac{1}{3}\rho G^2,$$

we obtain the value of $k$ by taking the temperature $\vartheta = 0$, thus finding

$$k = \tfrac{1}{3}\mathfrak{G}^2,$$

where $\mathfrak{G}$ denotes the mean molecular speed at the temperature $\vartheta = 0$; and it further necessarily follows that the square of the molecular speed $G$ increases in linear proportion with the temperature $\vartheta$, the relation between them being

$$G^2 = \mathfrak{G}^2(1 + a\vartheta).$$

We thus find that *the square of the molecular speed of a gas*, and therefore *the kinetic energy of its molecular motion, increases proportionally with the temperature*. The speed itself is given by

$$G = \mathfrak{G}\sqrt{(1 + a\vartheta)}.$$

This law is in complete agreement with the conclusion obtained in § 9 from Bernoulli's theory, viz. that *the kinetic energy of the molecular motion is the mechanical measure of heat and temperature*.

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[1] *Annales de Chimie et de Physique*, xliii. 1802, p. 137; *Gilb. Ann.* xii. 1802, p. 257.

[2] *Mem. of the Manch. Lit. and Phil. Soc.* v. 1802, p. 595; *Gilb. Ann.* xii. 1802, p. 310.

[3] See § 46.

## 15. Absolute Zero of Temperature

The law just found allows the position of the so-called *absolute zero* of temperature for gaseous bodies to be determined.

If heat is nothing else than the kinetic energy of molecular motion, the temperature at which a gas possesses no more heat must be identical with that at which its molecular motion has disappeared, and all atoms and molecules remain in a state of perfect rest.

The expression that has been found for the molecular speed $G$ shows that this speed vanishes when

$$1 + a\vartheta = 0.$$

If from the measures of Magnus,[1] Regnault,[2] Jolly,[3] Recknagel,[4] and others, which are all in agreement[5] with each other, we take 0·00367 for the value of $a$ in the case of air when the Centigrade scale is used, and put this in the last equation, we find

$$\vartheta = -272^\circ{\cdot}5 \text{ C.}$$

for the required temperature of the absolute zero. If we reckon temperature, not from the melting-point of ice arbitrarily chosen to start from, but from this absolute zero, then we obtain for the absolute temperature

$$\Theta = 272{\cdot}5 + \vartheta;$$

or, in the general case, for all scales in use we have

$$\Theta = a + \vartheta,$$

where the value of the constant $a$ is to be taken as the reciprocal of the coefficient of expansion[6] of air for the scale in question.

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[1] *Pogg. Ann.* lv. 1842, p. 25.

[2] *Mém. de l'Acad. de Paris*, xxi. 1847, p. 73; *Pogg. Ann.* lv. and lvii.

[3] *Pogg. Ann.* Jubelband, 1874, p. 82.

[4] *Pogg. Ann.* cxxiii. 1864, p. 127, table i.

[5] Mendelejeff, *Ber. d. deutsch. chem. Ges.* x. 1877, p. 81.

[6] [This requires definition; on the Fahrenheit scale, for instance, the coefficient of expansion is usually defined with reference to an initial volume at

Introducing this absolute temperature, we have for the mean molecular speed the formula

$$G = H\sqrt{\Theta},$$

where $H$ is a constant, the meaning and value of which are easily decided.[1] *The molecular speed,* therefore, *is a magnitude which increases proportionally to the square root of the absolute temperature.*

This determination of the absolute zero and of absolute temperature deserves the more notice, as it is the same, or very nearly the same, for all gases; for, as experiment shows, all gases have very nearly the same coefficient of expansion,[2] and therefore the position of the absolute zero is approximately the same for all gases.

A real meaning, however, is perhaps not to be ascribed to the zero[3] so found in the sense of its really denoting a temperature at which all molecular- and heat-motion ceases so that there is no more heat. For it is evident that if there is no more heat-motion there is also, according to our theory, no more tendency to expand, and therefore no body can remain in the gaseous state. The formula of Gay-Lussac's law cannot strictly be applied at such low temperatures, since possibly—and certainly for such gases as are condensed to liquids at temperatures above − 273° C.—this law loses its validity at some higher point, and another takes its place. The absolute temperature that has been introduced has therefore more the signification of an auxiliary mathematical function than of a physical reality.

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the freezing-point of water—viz. 32° F.—and in the case of air is taken to be $\frac{5}{9} \times 0{\cdot}003670 = 0{\cdot}002039$, whereas in the text an initial volume corresponding to $\vartheta = 0$ is required on all scales; so that for air on the F. scale we must take $a = 0{\cdot}002039 \div (1 - 0{\cdot}002039 \times 32) = 0{\cdot}002181$.—Tr.]

[1] [In fact, $H = 485 \div \sqrt{(272{\cdot}5 \times s)} = 29{\cdot}38/\sqrt{s}$ metres per second for the Centigrade scale.—Tr.]

[2] See § 32.

[3] On other determinations of the absolute zero of temperature see Gehler's *Physikalisches Wörterbuch*, x. p. 115.

## 16. Pressure and Energy

The formula found for the pressure of a gas,

$$p = \tfrac{1}{3}\rho G^2,$$

brings this magnitude into very close relation with another, namely, the kinetic energy of the molecular motions. Since the density $\rho$ measures the mass of gas contained in the unit of volume, the magnitude

$$K = \tfrac{1}{2}\rho G^2$$

is nothing else than the amount of kinetic energy possessed by the molecules in unit volume.

The simple relation deduced from these two formulæ, viz.

$$K = \tfrac{3}{2}p,$$

enables us to express the molecular energy by a magnitude which is directly amenable to observation. *The pressure and kinetic energy of a gas stand to each other in an invariable relation which is independent of the temperature.*

This simple relation is nothing else than an expression of the thought which underlies our theory. Both magnitudes, pressure and energy, have their origin in the molecular motion; they are even completely alike in their nature. Their difference consists only in the difference of the units in which their values are expressed. For the pressure which the walls of a gas-holder support forms also a measure of the kinetic energy of the contained gas.

Both magnitudes change proportionally to the absolute temperature, and we have

$$p = \frac{p_0}{\Theta_0}\Theta, \text{ and } K = \frac{K_0}{\Theta_0}\Theta,$$

where $p_0$, $K_0$ are the values of the pressure and kinetic energy per unit volume at the temperature of the freezing-point of water, which on the [Centigrade] scale of absolute temperature is

$$\Theta_0 = 272{\cdot}5.$$

On an ordinary scale of temperature wherein $\alpha$ is the coefficient of expansion [see note 6, p. 28] we have

$$p = p_0(1 + \alpha\vartheta), \text{ and } K = K_0(1 + \alpha\vartheta).$$

The latter formula, which is the mathematical expression for the proposition named several times already [§§ 9, 14], that the energy of the molecular motion is the mechanical measure of the temperature, shows that *the kinetic energy increases by the same amount for every degree of temperature.*

## 17. Dalton's Law for the Pressure of Mixed Gases

From this relation between the pressure and the kinetic energy of molecular motion a very important conclusion may be drawn if we extend our consideration to a gaseous medium containing molecules of different kinds, that is, to a gaseous mixture.

For such a mixture the calculation of the pressure exerted would be carried out in exactly the same way as was done in § 11 in the special case of a simple gas. The pressure on a surface is, in the more general case of a mixture of gases, also measured by the sum of the impulses of the molecules on a unit of area in a unit of time; its value is therefore represented by the total energy given up to the surface by all the different kinds of molecules present.

The formula for the value of the pressure exerted by a mixture of different gases therefore takes the slightly modified shape

$$p = \tfrac{2}{3}(K_1 + K_2 + \ldots),$$

where the magnitudes denoted by $K$ are the values of the kinetic energy per unit volume of the molecular motions in the single components of the mixture, and are given by

$$K_1 = \tfrac{1}{2}\rho_1 G_1^2, \quad K_2 = \tfrac{1}{2}\rho_2 G_2^2, \ldots$$

$\rho_1, \rho_2, \ldots$ being the densities of these components, and $G_1, G_2, \ldots$ the mean speeds of their molecules.

But the values of the pressures which the components of the mixture would severally exert if separately occupying the volume of the mixture are

$$p_1 = \tfrac{2}{3}K_1, \quad p_2 = \tfrac{2}{3}K_2, \ldots;$$

whence

$$p = p_1 + p_2 + \ldots,$$

or *the pressure exerted by the mixture is equal to the sum of the pressures separately exerted by its several components.*

Thus the law found by Dalton[1] for the pressure of mixed gases, and confirmed and defended by Henry[2] against many attacks, follows as a necessary consequence from the assumptions underlying our theory. Of these one was assumed by Dalton, viz. that molecules of different gases act on each other neither attractively nor repulsively, and it is the most important for our present case; for it is this assumption which entitles us to consider that we have to take into account kinetic, and not also potential, energy.

That this assumption is not absolutely exact, but only approximate, has already several times been pointed out [§§ 4, 8]. Just as Boyle's law, this of Dalton can have only a limited validity.[3]

Dalton's hypothesis, that molecules of different gases neither attract nor repel each other, is often taken to mean that they do not exert pressure on each other. This is quite inadmissible on our theory, for molecules of different kinds moving about in a given volume collide with each other just as much as if they were of the same kind, and, consequently, must exert pressure on each other, as pressure is nothing but the sum of the actions produced by impact.

And this reading of Dalton's hypothesis is also in disagreement with experiment; for different gases do really exert pressure on each other, as has been proved by manifold observations.[1]

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[1] *Mem. of the Manch. Lit. and Phil. Soc.* v. 1802, p. 535; *Gilb. Ann.* xii. 1802, p. 385.

[2] *Nicholson's Journal*, viii. 1804, p. 297; *Gilb. Ann.* xxi. 1805, p. 393.

[3] Regnault, *Mém. de l'Acad.* xxvi. 1862, p. 256; Andrews, *Phil. Trans.* clxxviii. 1887, p. 45; Cailletet, *Journ. de Phys.* [1] ix. 1880, p. 192; Galitzine, *Ueber das Dalton'sche Gesetz*, Inaug. Diss. Strassburg, 1890; *Wied. Ann.* xli. 1890, pp. 588, 770; *Gött. Nachr.* 1890, No. 1; U. Lala, *Comptes Rendus*, cxi. 1890, p. 819, cxii. 1891, p. 426; *Naturw. Rundschau*, vii. 1892, p. 188.

The meaning of this law is simply that a mixture of two or more gases possesses the same amount of kinetic energy as its components taken together, and the correctness of this fact is proved by the observation that if two gases at the same temperature and pressure are mixed together there is neither generation nor absorption of heat.

## 18. Heating by Compression

Remembering that the pressure, energy, and temperature of a gas increase together in constant ratios, we have at once an explanation of the fact that the temperature of a gas is raised by compression and lowered by expansion. Even without employing the assumptions of the kinetic theory, it is not difficult to see that a diminution of volume caused by heightened pressure must be bound up with an increase of energy, and that part of this energy may be transformed into heat; expansion, on the other hand, requires an expenditure of mechanical or heat energy to overcome the opposing external pressure. All, however, is not explained by this general consideration. We obtain a deeper insight into the nature of the phenomenon when we investigate more closely the nature of the molecular motion in a gas that is being compressed or expanded.

Let the gas be in a cylinder which is closed by a movable piston. To keep this in equilibrium a pressure must be exerted upon it which will balance the action of the molecules impinging on it. But when an excess of pressure acts on the piston from the outside, the piston is driven into the cylinder; and during this motion of the piston the forces that come into play in the collisions with the oppositely moving molecules are increased. The molecules are, therefore, thrown back with greater vigour, and consequently attain a greater speed on rebound from the moving piston than if they strike it when fixed. But since the kinetic energy of the molecular motion is nothing but heat, it is obvious that the compressing motion of the piston communicates heat to the gas.

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[1] For instance, Lamont, *Pogg. Ann.* cxviii. 1863, p. 168; *Schlömilchs Zeitschrift*, viii. 1863, p. 72, ix. 1864, p. 439; Bunsen, *Gasometrische Methoden*, 1857, p. 209; 2nd ed. 1877, p. 267; O. E. Meyer and F. Springmühl, *Pogg. Ann.* cxlviii. 1873, p. 540.

The reverse occurs when the pressure on the piston is so small as to be overcome by the impacts of the molecules. The piston then moves in the same direction as the molecules that strike it, which therefore attain a less speed by the impact, as they give part of their former momentum to the piston. The gas consequently cools in doing work by pushing the piston out.

In this way the heating of a gas by compression was explained by Krönig[1] and Clausius.[2] A mathematical theory of the phenomenon has been given by Woldemar Voigt.[3]

It has been shown by Clausius that the heat produced by pressure can easily be calculated on the grounds of our theory, and that it is equal to the work done. In a rather later memoir[4] he gives a proof which we here reproduce.

We will, for simplicity, continue to use Joule's procedure, described in § 10, and therefore assume not only that all molecules possess the same mean speed $G$, but also that only one-third of the molecules are to be taken into account in calculating the impacts on a wall of the containing vessel. This assumption is admissible if the compression takes place so slowly that the disturbance of the equilibrium has always time at once to subside. With this supposition the number of molecules which in unit time meet unit area of the wall of the vessel is $\frac{1}{6}NG$, by § 12, and the number therefore in unit time which strike the surface $F$ of the piston is

$$\frac{1}{6}FNG.$$

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[1] *Grundzüge einer Theorie der Gase*, 1856; also *Pogg. Ann.* xcix. 1856, p. 315.

[2] *Pogg. Ann.* c. 1857, p. 365; *Abhandl.* pt. 2, 1867, p. 242.

[3] *Gött. Nachr.* 1885, No. 6, p. 228. See Natanson, *Wied. Ann.* 1889, xxxvii. p. 341.

[4] *Mech. Wärmetheorie*, iii. 1889–91, § 14, p. 29.

Each of these molecules would, after impact, rebound in the opposite direction with unchanged speed if the piston were at rest. But let the piston which compresses the gas move forward with a speed $a$, in the direction opposite that of the molecules which strike it with speed $G$. The strength of the rebound is thereby increased in the ratio in which the relative velocity $G + a$ exceeds the molecular speed $G$. A rebounding molecule therefore experiences in the impact an impulse, which is not $2mG$ as before, but the greater one, $2m(G + a)$, which results from its losing its initial speed $G$, and gaining the speed $G + 2a$ in the opposite direction; its kinetic energy therefore increases during the impact by

$$\tfrac{1}{2}m(G + 2a)^2 - \tfrac{1}{2}mG^2 = 2ma(G + a).$$

This we may with sufficient exactness replace by $2maG$, since we have assumed that the compression goes on so slowly that every disturbance of the molecular motion at once subsides; for we thereby also assume that the speed $a$ of the piston is negligible in respect of the speed $G$.

Since each molecule gains this amount of energy at every collision, the whole gain of energy by the gas in unit time due to the impact of $\frac{1}{6}FNG$ molecules, as above, on the piston is given by

$$\tfrac{1}{3}NmG^2Fa.$$

This product has a very simple meaning; for the pressure of the gas which the piston has to overcome is $p = \frac{1}{3}NmG^2$, by § 11, and the diminution which the volume $V$ of the gas experiences in unit time is $\delta V = Fa$, as in this time the piston moves through the length $a$ in the cylinder, the sectional area of which is $F$, and therefore the expression found for the increment of energy is

$$\tfrac{1}{3}NmG^2 . Fa = p\,\delta V.$$

It is thus proved that the kinetic energy gained by the gas during the compression is equal to $p\,\delta V$, the work which the piston must do to overcome the pressure of the gas.

## 19. Cooling by Expansion

In exactly the same manner the reverse phenomenon may be explained by the kinetic theory, viz. that a gas must cool when it does work by expanding, and that it thereby loses an amount of molecular energy equal to the work done.

If by its pressure the gas pushes back the piston with a speed which, as before, we will denote by $a$, the molecular speed of a molecule which impinges on the piston diminishes from $G$ to $G - 2a$, and there passes therefore from the molecule to the piston at each impact the energy $2maG$. Thus the molecules that strike the piston in unit time, $\frac{1}{6}FNG$ in all, lose the total energy

$$\tfrac{1}{6}FNG \,.\, 2maG = \tfrac{1}{3}NmG^2 \,.\, Fa = p\,\delta V,$$

which is the work done by the gas in expanding through the volume $\delta V$ against the pressure $p$.

The rise of temperature that accompanies the compression of a gas and the fall that results from its expansion can from this be easily calculated if the value of the specific heat of the gas at constant volume is known. We have only to apply to this problem the general theorem of thermodynamics that heat and energy are equivalent to each other. If we represent by $A$ the heat which is equivalent to a unit of work, $Ap\,\delta V$ is the heat which is added to the gas during the compression of its volume from $V$ to $V - \delta V$ or which leaves it during the expansion from $V$ to $V + \delta V$. We can otherwise express this heat in terms of $\delta\vartheta$, the change produced in the temperature $\vartheta$. If $c$ is the specific heat at constant volume, $\rho V$ the mass of the gas in the cylinder, and therefore $\rho Vc$ its heat-capacity, the relation between the heat produced by compression and the corresponding rise of temperature is

$$\rho Vc\,\delta\vartheta = -Ap\,\delta V,$$

and this holds good too for the case of the gas cooling by expansion. The negative sign has to be introduced into the formula to indicate that an increase of volume corresponds to a diminution of temperature, and *vice versâ*. The change of temperature which occurs is therefore

$$\delta\vartheta = -\frac{Ap}{c\rho}\,\frac{\delta V}{V}.$$

Here $c$ denotes the specific heat at constant volume and not that at constant pressure. That this is so we shall easily see by again analysing the procedure. Without transgressing the law of the conservation of energy we can thus picture the transaction; that the work of compression $p\,\delta V$ first produces a *progressive* velocity $a$ of the gas, the volume being diminished without the to-and-fro motions of the molecules being altered, and that then, on the piston ceasing to move forwards, the energy of the progressive motion communicated to the gas is transformed into heat without change of volume by the collisions of the molecules. In the calculation, therefore, it is the specific heat at constant volume that is to be taken into account.

## 20. Vaporisation

Many gaseous bodies are condensable into liquids by application of pressure only, without the necessity of removing heat from them. Such substances are called vapours, in contradistinction to gases proper.

The cause of liquefaction by pressure alone we can only look for in the forces of cohesion. If the molecules of a gas are brought nearer each other by increase of pressure, those forces are exerted in greater degree; and it may happen that, if the molecules are brought near enough together, their action is so much increased that the molecules cannot separate any more from each other. For this it is necessary that the kinetic energy of the molecules shall be no longer sufficient to overcome the energy of the cohesive forces. If this limit is reached, the vapour begins to change into liquid.

There is now a condition of equilibrium, in which one part of the substance remains liquid and another hovers above the liquid as vapour. In this vapour the molecules in general move in straight lines, except when two approach very near to each other. In consequence of this linear motion it must often happen that a molecule of vapour strikes against the surface of the liquid; in this case, under favourable conditions, it may be held there by cohesion.

In the liquid, too, the molecules are not at rest, but are in as brisk motion as in the vapour, but not in straight lines. In consequence of this motion it may happen that a liquid particle gets out of the range of the forces of cohesion and passes again into the vapour.

There is, therefore, a continuous interchange of molecules between liquid and vapour, and, since there is equilibrium, as many molecules must on the average pass from the vapour into the liquid as from the liquid into the vapour.

On considering that this equilibrium between liquid and vapour extends also to temperature, we see that not only as much mass but also as much energy necessarily passes from the liquid to the vapour as from the vapour to the liquid. The same number of molecules therefore carry over the same amount of energy from the one state of aggregation to the other, and this is only possible if *the energy of a molecule is as great in the liquid as in the vapour*.

In this theorem we have to remember that we are not dealing with kinetic energy only, but in the case of liquid molecules with the sum of their kinetic and potential energy.

This equilibrium will only be maintained, however, when the vapour has a certain density, so that there is a sufficient number of molecules to bombard the surface of the liquid. Such a vapour is called a *saturated vapour*.

If liquid is introduced into a vessel in which there is at first no vapour of this substance, vapour at once begins to form in consequence of the heat present. Molecules detach themselves from the liquid surface and move about as molecules of vapour in the free space above. Such a separation of a molecule from the liquid left behind takes place the more easily the greater the energy which the escaping molecule possesses. With the molecules that have darted off, therefore, the liquid loses a sum of energy which is greater than that which on the average falls to these molecules, and thus for those that are left behind there remains a less amount of energy than they possess hitherto on the average. It is thus explained on our theory that *a liquid cools by vaporisation.* The heat that has disappeared has gone in doing the work of expansion.

## 21. Absorption and Adsorption

Quite the same state of things occurs when a gas or vapour is dissolved in a liquid which is not of the same substance as occurs in the phenomenon of absorption. In this case the gaseous substance throngs into the liquid in consequence of the motion of its molecules, and is held fast by the attraction exerted on it by the liquid; and this process goes on until equilibrium between evaporation and condensation occurs.

On the absorption of a gas by a liquid, heat is developed which is greater in amount than the latent heat of vaporisation. As the latter is equal to the sum of the kinetic energy of the molecules of the gas and the potential energy required to overcome the cohesion in the liquefied gas, it follows that still more energy than this is required to separate the gas from the liquid which has absorbed it. Hence there is no doubt as to the existence of an attraction of the gas by the liquid.

If the force with which the liquid, when in the state of a saturated solution, retains the gas were as great as if the liquid were pure, the number of the molecules of gas absorbed by the liquid would be exactly proportional to the number of molecules remaining above it in the gaseous state, and Henry's law, that the mass of gas absorbed increases proportionally to the acting pressure, would hold strictly. But as this supposition cannot be accurate when large masses are absorbed, Henry's law can only approximately represent the truth.

A rise of temperature also increases the energy of the molecules in the absorbed gas; they will, therefore, at a higher temperature come oftener into a position of being able again to escape from the liquid. Therefore the higher the temperature the less gas will be absorbed, as observation has taught.

Molecules of a gas can also be held fast by a solid body just as by a liquid, porous bodies especially being able to condense considerable masses of gas. In other cases the mass condensed increases with the extent of surface of the body, and we must therefore assume that only the surface layers are active in causing condensation by the attractive forces they exert. On this account it has been thought necessary to introduce a new name and designate the phenomenon as *Adsorption* when the condensation is caused by a solid body. It differs, however, in nothing else from absorption in liquids; on the contrary, everything that has been stated about absorption can be ascribed to adsorption without further remark. One such fact is that by adsorption also can considerable heat be developed, as, for instance, in Döbereiner's lamp, on the condensation of hydrogen by spongy platinum.

# CHAPTER III

## *MAXWELL'S LAW*

### 22. Unequal Distribution of Molecular Speed

THE mean value of the molecular speed given in § 13 is not the arithmetic mean of all the different values of the speeds with which individual molecules move. The magnitude $G$—by which the mean value in question is denoted—has been defined in § 10 to be such that the mean energy of the molecules which strike against the wall would be unaltered if all of them possessed this same speed $G$ instead of their actually different speeds. From this it results that with that equalised distribution the gaseous medium retains the same energy and exerts the same pressure as with its actual unequal distribution.

So long as we are concerned only with the calculation of the pressure and energy, therefore, it is sufficient to ascribe this mean speed to all molecules. But if we wish to investigate more nearly the character of the gaseous state, we have to ask ourselves whether a difference in the values of the speeds is possible, and, further, how these different speeds are actually distributed among the molecules.

That the equilibrium of a swarm of gaseous molecules in no way depends on the speed of all the molecules being the same, and that, on the contrary, there must really be a non-uniform distribution of speed among the molecules, can be seen without calculation. For it is easy to prove that if all the molecules had exactly equal speeds at any moment, this distribution of speed would be at once disturbed, and in place of it a non-uniform distribution would be established.

Consider, for instance, the case of a moving particle being struck perpendicularly to the direction of its motion and so that the direction of the blow passes through its centre of mass; then the striking particle will cede part of its speed to the struck particle, which, as it experiences no resistance in the direction of the path it has thus far traversed, will retain its own motion undiminished, and, therefore, receiving in addition a further speed from the striking particle, will move more quickly than before the collision, and in changed direction, while the other moves more slowly, since it must lose speed.

This example shows that in such an aggregation of molecules as we assume in gaseous bodies in our theory the speeds of the individual molecules cannot be equal in the state of equilibrium. Equilibrium can, therefore, only consist in a condition of continuous interchange of speed between every pair of colliding particles, every particle now gaining and now losing, its velocity being now big and now little, and changing as often in direction as in magnitude.

It is for this continuous change of motion of the particles as they dash about that we have to investigate the law.

## 23. The Applicability of the Calculus of Probability to the Kinetic Theory

The attempt to deduce a law for something that is subject only to chance may seem singular and strange, but this should not deter us from undertaking a research which touches the very core of the kinetic theory.

This theory, indeed, seeks for the cause of regular phenomena and regular properties of gaseous media in irregular tumultuous motions of the molecules. We have here to look at the observed facts, not as direct necessary consequences of unchangeable laws as is usual, but as the result of a large number of elementary processes which are subject to no law but that of chance. And yet all phenomena occur in unchangeable regularity.

This is certainly a very uncommon position, but it is by no means unwarranted, and it is also not in the least limited to this theory only. During every chemical reaction the atoms which separate and combine again must at first move confusedly about in irregular disorder till the new regular arrangement is found. A still more striking example of a regular law arising from chance events is afforded by meteorological phenomena, the varied change of which follows a law that is clearly recognisable from the means of long periods.

In all these cases, and in our theory as well, the regularity arises only from the great number of the elementary processes from which it results. If this number were not so great, the result in similar cases would not always be absolutely and fixedly one and the same, but there would be different results conceivable of more or less probability. But the greater this number, the greater the probability that of all possible consequences a single perfectly definite one would occur just as if it were directly caused by the operation of a fixed law of nature instead of by the play of numberless casual events.

Applied to our theory this general view teaches that in a really infinite number of molecules of gas a condition must exist, the law of which must admit of recognition and even of mathematical expression, in spite of the chance character of the motion of each individual molecule. We must therefore be able to determine how many molecules per thousand, say, taken at random from the countless swarm, have a speed of a definite magnitude, or, in somewhat different words, we must be able to express numerically the chance that any given molecule in a region filled with an infinite host of molecules should attain a speed of given value.

In a gaseous mass consisting of a finite number of molecules this condition of simple regularity will not be attained, as in the case of an infinite number—at least not at every instant. In a finite system this law shows itself only if all the states which occur with continual change in the course of longish periods are taken into account together. The particular condition of regularity which is exhibited at every moment by an infinite swarm determines also for a finite number of molecules its mean state during a considerable period.

The arrangement that changes from moment to moment and represents the distribution of the different speeds among a limited number of molecules, oscillates therefore about a mean regular state, and in such wise that the result which ensues in the course of a considerable time is the same as if that regular state had existed at each moment. In the calculation of the result we may therefore consider that regular distribution of speeds as always existing instead of the actual circumstances of constant change.

## 24. Maxwell's Law

The law which regulates this distribution of speeds among the gaseous molecules was discovered by James Clerk Maxwell,[1] who thus made it possible to calculate, by strict mathematical methods, the mean values of the speeds which hitherto had been only estimated, and a knowledge of which was necessary for the development of the theory of gases.

Maxwell's law of distribution, the theoretical foundation of which rests on the calculus of probabilities, agrees exactly in form with another law which is also founded on this calculus. *The possible values which the components of the molecular velocities can assume are distributed among the molecules in question according to the same law as the possible errors of observation are by the method of least squares distributed among the observations.*

According to this law the equilibrium of a gas depends, of course, as was to be expected, in no way upon equality of motion in all the particles. All values between 0 and ∞ occur for the components of velocity, and in such fashion that small values occur oftener than large ones, just as according to the method of least squares errors of small magnitude should happen oftener than large ones.

In order to give an idea of this law without having recourse to mathematical formulæ I will quote a few figures.[2]

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[1] *Phil. Mag.* [4] xix. 1860, p. 22; *Scientific Papers*, i. p. 377.

[2] Obtained from the values of the integrals

$$\int_0^1 dz\, e^{-z^2} = 0{\cdot}74682, \quad \int_1^2 dz\, e^{-z^2} = 0{\cdot}13525, \quad \int_2^3 dz\, e^{-z^2} = 0{\cdot}00413.$$

If 10,000 molecules move with such velocities that their components in any given direction lie in magnitude between 0 and a certain value $W$ (see § 27), then there are only 1,811 for which this component lies between $W$ and $2W$, and but fifty-five with a value between $2W$ and $3W$ for the component. The small values therefore predominate in remarkably large proportion, and the probability of larger values of a component of the molecular velocity, just as that of large errors of observation, is vanishingly small.

In this form the law expresses the frequency of occurrence of the values which the three components of the velocity assume. We shall show later on, in § 26, how the probability of a particular value of the resultant velocity of a molecule can be deduced from it.

As has been already mentioned, Maxwell's law can be employed in two ways. First of all it tells us how many of a certain number of molecules move with a given velocity at the same moment; but, secondly, it serves equally well to give the frequency with which one and the same particle attains a given velocity in consequence of its encounters with other particles.

## 25. Proof of Maxwell's Law

Several demonstrations resting on different footings have been tentatively given for this law of distribution of molecular speeds.

Its discoverer, J. Cl. Maxwell, first[1] proved it by the assumption of a principle which, though true, itself needs proof.[2] Since Maxwell himself recognised this defect, he later gave a second proof,[3] the basis of which is subject to no doubt. Since the state of equilibrium with which the law is concerned is not disturbed by encounters between the molecules, but is continuously maintained, every change produced by collision must at once be cancelled by other collisions. A velocity of a particular magnitude and direction will therefore result from one collision as often as it will be destroyed by another; and from this principle, together with the laws of collision, Maxwell's law may be established.

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[1] *Phil. Mag.* [4] xix. 1860, p. 22; *Scientific Papers*, i. p. 377.

[2] See the end of § 14* of the Mathematical Appendices.

[3] *Phil. Trans.* clvii. 1867, p. 49; *Phil. Mag.* [4] xxxv. 1868, p. 185; *Scientific Papers*, ii. p. 43.

L. Boltzmann[1] completed and perfected this proof by employing stricter mathematical work, and thus removing just ground for doubt. A further step forward we owe to H. A. Lorentz,[2] who raised a new objection and improved the calculation, thereby inciting Boltzmann[3] to again give a new proof, which proof may now be considered as quite free from objection.

Further, Kirchhoff has given a proof of the law in his Lectures[4]; but against this, too, according to a remark of Boltzmann,[5] objection may be made.

In a different way the proof of this law was attempted in the first edition of this book. The weak points of this attempt were removed by N. N. Pirogoff,[6] and a varied form of Pirogoff's proof is given in the second of the Mathematical Appendices.

These mathematical proofs cannot be repeated here, nor should we attempt here to give them; I will only indicate a striking point that arises from them.

Since the law of distribution which we are looking for is concerned with the state which in time results from the encounters between molecules, we might expect that a knowledge of *what occurs during the encounters* might be necessary in order to find the law. It would seem that we ought to know the law of collision for molecules if we would calculate the final result of the collisions; and apparently we must therefore know whether the molecules behave during collision as elastic bodies, or whether their collisions occur as those between hard or soft bodies.[7]

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[1] *Wiener Sitzungsber.* lviii. 1868, p. 517; lxvi. 1872, p. 275.

[2] *Ibid.* xcv. 1887, p. 115.

[3] *Ibid.* xcv. 1887, p. 153.

[4] *Vorlesungen über mathematische Physik*, iv. (*Theorie der Wärme*, herausgeg. von Planck), 1894, p. 142 (14th Lecture).

[5] *Münchener Sitzungsber.* xxiv. 1894, p. 207. *Ibid.* (Planck) p. 391.

[6] *Journal der russ. physik.-chem. Ges.* xvii. 1885, pp. 114–135, 281–313.

[7] A discussion of the question how far the laws of elastic collision are applicable to molecules of gas is given in Chapter X.

But the knowledge of the laws of collision proves to be quite unnecessary for the proof of Maxwell's law. So little indeed is it necessary, that Maxwell was able in course of time to change his views on this point without having to upset or reject the theory established by him. At first he thought it probable that two colliding molecules, just as two hard elastic bodies, would, after the collision in which they might have come into actual contact, be hurled apart by a suddenly arising and vanishing force. But later, on grounds which I shall examine in Chapter X. § 123, in discussing the molecular forces, he declared it more probable that two molecules of gas act on each other with repulsive forces, which, varying inversely as the fifth power of the distance, are insensible at greater distances, but at smaller suffice to force apart two molecules coming very near each other. We may hold either the one view or the other without prejudicing the validity of these proofs.

This shows that for the purpose we have first in view it would be superfluous to indulge in speculations on the character and the laws of the forces that come into play during the collision of molecules. A decision in favour of a particular hypothesis would only diminish the value of Maxwell's law, as it would seem to limit its validity. For the law is valid independently of all hypotheses.

For the proof of Maxwell's law it is therefore sufficient, as Boltzmann[1] has already recognised, to impress the quite general, and on that account indubitable, propositions of analytical mechanics ; Maxwell too has made use of these alone. So in the proof given in the Mathematical Appendices (§ 10*) it stands out clearly that Maxwell's law needs the assumption of these general propositions only.

The most important of these propositions is that of the *Conservation of Energy*. The admissibility of its application to molecular motion will not be questioned, but there is one precaution to mind. If the molecules do not consist of single massive points, but are made up of combinations of several atoms, we have to take into account not merely velocity of the molecule being zero. We shall rather obtain a value differing from zero in determining the mean of the absolute values of the molecular speed without reference to direction, in all those cases in which one of the three components is zero.

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[1] *Wiener Sitzungsber.* lxiii. 1871, pp. 397, &c.

Maxwell's law must therefore be differently expressed than it is in § 24, when it has reference not to the components of the velocity, but to the actual speed itself. We can then explain the law as follows :—

There is a *most probable* value of the speed which occurs more frequently than any other. Other values of the speed, whether greater or less, occur the oftener or are the more probable the nearer they approach to equality with the most probable. Infinitely great as well as infinitely small values of the speed have infinitely small probability. Molecules at rest, therefore, are infinitely seldom to be met with.

The connection between the two different forms of the law may be clearly illustrated by a comparison employed by Maxwell[1] in a lecture.

If practised marksmen shoot at a target, the hits are most crowded together near the centre, and there are but few shots near the edge; the marks are approximately represented by the figure on page 51. In this case, too, the distribution of the hits follows the same law which Maxwell has found for the molecules of gas, viz. the law of errors; for a shot at the target is an attempt to hit the centre, just as a measurement is an attempt to hit the true value of the measured magnitude. Small deviations from the centre are therefore more probable than large ones in target practice also. The shots can deviate to right or left, above or below, and thus both horizontally and vertically. We have therefore in this case two components of deviation to distinguish, a horizontal and a vertical; and for each component the value zero is the most probable, since if we draw a series of parallel lines, say vertically, on the target, that one which passes through the centre passes also through more shot-marks than any other. But what is true for the components cannot be immediately transferred to the resultant deviation from the centre. The points that are equally distant from the centre do not lie on a straight line, but on a circle described about the centre; and the circle which passes through the most shot-marks is by no means one of the innermost circles of the target, for the inner rings are too small to contain many marks—in fact, the circle passing through the most shot-marks lies on a ring of medium size. The same relations hold also for the values of the speeds and of the components of velocity which occur the most frequently among the molecules of gas.

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[1] 'On the Dynamical Evidence of the Molecular Constitution of Bodies,' *J. Chem. Soc.* xiii. 1875, p. 438 ; *Nature*, xi. p. 357 ; *Scientific Papers*, ii. p. 418.

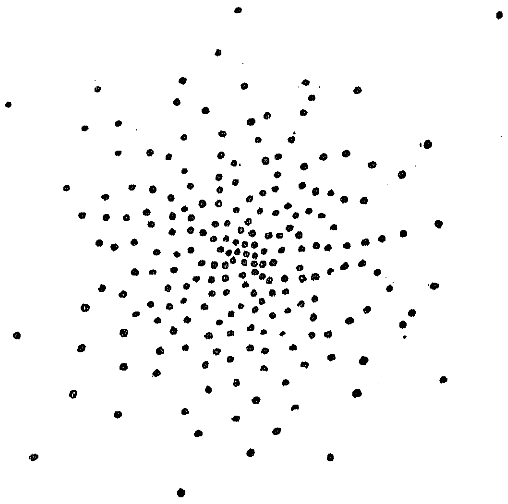
FIG. 1

A more exact representation of the unequal probability of different values of the speed is given by the curve on page 52, the course of which shows us the law regulating the number of molecules which move with a given speed. In the figure the function which determines the frequency of a value is represented by a curve with the equation

$$y = 4\pi^{-\frac{1}{2}}x^2e^{-x^2}.$$

This construction means that the magnitude of the ordinate $y$ of the curve is equal to the probability of a speed whose magnitude is equal to that of the abscissa $x$, and for the unit of speed that value is chosen which is the most probable.

This graphic representation of the law lets us easily see that the values of the speed that occur with any considerable frequency are only slightly different from that of greatest probability, whence we might conclude that the idea of all the molecules possessing equal speed is really approximately admissible. For a speed which is three or even only two and a half times as great as the most probable speed has an almost vanishing probability, as a glance at the figure shows, so that no speeds can in fact occur which considerably surpass this value. And this is the case, too, with markedly smaller speeds.

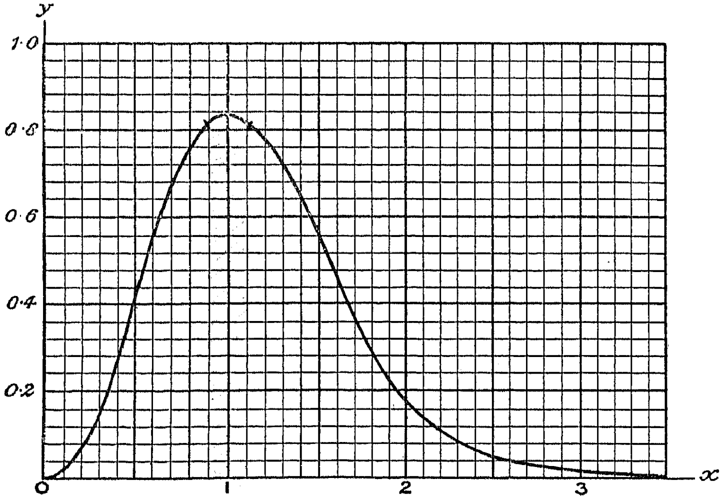

FIG. 2

Pirogoff[1] has therefore gone so far as to assume that the values of the molecular speed which really occur lie between fixed limits, both the very large and the very small values of the speed being cut out by some equalising action such as a resistance or something of that kind. We may, in fact, as we easily see from the curve, determine such

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[1] *Fortschr. d. Physik*, 1886, 42. Jahrg. 2. Abth. p. 241.

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limits that the variable values lying between them give the same mean kinetic energy as if all the values are possible. We have merely to take one limit on the ascending and the other on the descending branch of the curve at corresponding places.

The probability that the speed of a molecule lies between given limits is represented on the figure by the area included between the curve, the axis of abscissæ, and the ordinates corresponding to the limits. In this way we find, for instance, that the probability of a value between 0·9 and 1·1 of the most probable value is given by $0{\cdot}2 \times 0{\cdot}8 = 0{\cdot}16$ ; that is, 16 molecules out of every 100, or 1 out of every 6, have speeds which deviate less than 10 per cent. from the most probable value. There are, on the contrary, as we similarly find, about 9 molecules in every 100 which possess within 10 per cent. of half the most probable value, and about 11 in 100 with a speed equal, within the same limits, to $1\frac{1}{2}$ times this value. There are, further, but 3 in 100 with a speed 4 times less than, and scarcely more than this number with a speed twice as great as, the most probable.

## 27. Mean Value of the Speed

These numbers teach us, as indeed does a glance at the curve, whose ascending branch is steeper than its descending, that the number of particles, whose molecular speed is greater than the most probable, surpasses that of the particles which move with a speed less than the most probable. The most probable speed is therefore not also the arithmetical mean of the various speeds, but *the mean value of the speed is greater than the most probable.* Similarly the mean value of the molecular energy is greater than the energy of a molecule which moves with the most probable speed.

The values of the molecular speed, which we have calculated in § 13 by Joule and Clausius' method, from the pressure exerted by gases, are, therefore, not at all the most probable values of the speed of the molecular motion. Indeed, we cannot strictly regard them as correct means of the various speeds; at least, they are not the *arithmetic* means, but the values of the speed which correspond to the arithmetic means of the energy of the different particles. (See § 10.)

By a simple mathematical consideration we may easily see that the method by which Joule and Clausius calculated the mean values of the molecular speed must in all cases give numbers which are greater than the real arithmetic means. Consider $n$ particles moving respectively with the speeds $a, b, c \ldots$; the mean value of these different speeds is then

$$\Omega = (a + b + c + \ldots)/n.$$

Calculating also the mean value of the molecular energy of a particle,

$$E = \tfrac{1}{2}mG^2,$$

wherein $m$, as before, represents the molecular mass, and $G$ the mean value of the speed, we obtain

$$E = \tfrac{1}{2}m(a^2 + b^2 + c^2 + \ldots)/n,$$

so that the mean value $G$ of the speed introduced by Joule and Clausius has the signification

$$G^2 = (a^2 + b^2 + c^2 + \ldots)/n.$$

Comparing this expression with

$$\Omega^2 = (a^2 + b^2 + c^2 + \ldots + 2bc + 2ca + 2ab + \ldots)/n^2,$$

which, as we see from the known relation

$$a^2 + b^2 > 2ab,$$

leads to

$$\Omega^2 < (a^2 + b^2 + c^2 + \ldots + b^2 + c^2 + c^2 + a^2 + a^2 + b^2 + \ldots)/n^2,$$

or, since each square occurs $n$ times in the numerator, to

$$\Omega^2 < (a^2 + b^2 + c^2 + \ldots)/n,$$

we find

$$\Omega < G;$$

that is, *the arithmetic mean value $\Omega$ of the speed is less than the mean value $G$ calculated by Joule and Clausius from the mean kinetic energy.*

If Maxwell's law is true, this relation, which holds in general between the two mean values, takes the following simple form that is equally true for all gases, viz. (see § 19* of the Mathematical Appendices) :—

$$\begin{aligned}\Omega &= G\sqrt{(8/3\pi)}\\ &= 0{\cdot}9213\,G,\end{aligned}$$

which, with extreme approximation, may be written

$$\Omega = \tfrac{12}{13}\,G.$$

Joule and Clausius' values are therefore greater than the arithmetic means of the molecular speeds by about a twelfth part.

The latter may just as easily as the former be calculated from the value of the pressure; for the formula for the pressure $p$ given by Joule and Clausius (§ 13), viz.

$$p = \tfrac{1}{3}\rho G^2,$$

where $\rho$ denotes the density of the gas, may be replaced by

$$p = \tfrac{1}{8}\pi\rho\Omega^2,$$

from which the arithmetic mean values $\Omega$ of the molecular speed for different gases may be calculated, as has already been done in a Latin dissertation[1] that I published in 1866.

Further, for the calculation of the *most probable* value $W$ of the speed, according to Maxwell's theory, we have the formula

$$W = \tfrac{1}{2}\pi^{\frac{1}{2}}\Omega = G\sqrt{(2/3)}\,;$$

the value $W$ is, therefore, smaller than both the others, and stands to them in a ratio which is the same for all gases.

Closely related to this most probable value is a third mean value of the speed, which is called the value of *mean probability*, or, more shortly, the *mean probable* value. The signification of this value, which I denote by $O$ in § 19* of the mathematical theory, is that there are as many particles with speed less than $O$ as there are particles with speed greater than $O$. Its value lies between $W$ and $\Omega$, and we have

$$O = 1{\cdot}09\,W = 0{\cdot}96\,\Omega.$$

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[1] Inaugural dissertation, *De Gasorum Theoria*, Vratislaviæ 1866.

## 28. Values of the Speeds

In order to give a clearer idea of these relations I have calculated a few examples of numbers, and more especially for the two gases which are the most important constituents of atmospheric air, namely, oxygen and nitrogen. The densities of these gases, according to Jolly,[1] are

$$\rho = 0{\cdot}0014291 \text{ for oxygen}$$
$$= 0{\cdot}0012576 \text{ ,, nitrogen,}$$

when at 0° under the pressure of a mercury column 0·76 m. high at Munich, where the acceleration of gravity is 9·8069 m. per sec. per sec. We therefore obtain for the *Joule-Clausius mean values* at 0°

$$G = 461{\cdot}2 \text{ m. per sec. for oxygen}$$
$$= 491{\cdot}7 \text{ ,, ,, nitrogen,}$$

which completely agree with the values given in §13, as deduced by Clausius from Regnault's observations. From Maxwell's law we obtain for the *arithmetic means* of the molecular speed at 0°

$$\Omega = 424{\cdot}9 \text{ m. per sec. for oxygen}$$
$$= 453{\cdot}0 \text{ ,, ,, nitrogen.}$$

The *mean probable* values at 0° are

$$O = 409{\cdot}5 \text{ m. per sec. for oxygen}$$
$$= 436{\cdot}6 \text{ ,, ,, nitrogen,}$$

and, finally, the *most probable* values of the speed at 0° are

$$W = 376{\cdot}6 \text{ m. per sec. for oxygen}$$
$$= 401{\cdot}4 \text{ ,, ,, nitrogen.}$$

Lord Rayleigh[2] found hydrogen to be 15·884 times lighter than oxygen, and consequently for hydrogen at 0°

$$G = 1838{\cdot}2 \text{ m. per sec.}$$
$$\Omega = 1693{\cdot}6 \text{ ,,}$$
$$O = 1632{\cdot}2 \text{ ,,}$$
$$W = 1500{\cdot}9 \text{ ,,}$$

The law of the unequal distribution of different speeds is shown by the following numbers. Of 1,000 molecules of oxygen at 0°

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[1] *Abh. d. Akad. zu München*, xiii. 2. Abth.; *Wied. Ann.* vi. 1879, p. 520.

[2] *Proc. Roy. Soc.* xxiii. 1888, p. 356.

| | | | |
|---|---|---|---|
| 13 to 14 | molecules have a speed | below 100 | m. per sec. |
| 81 „ 82 | „ „ | from 100 to 200 | „ |
| 166 „ 167 | „ „ | „ 200 „ 300 | „ |
| 214 „ 215 | „ „ | „ 300 „ 400 | „ |
| 202 „ 203 | „ „ | „ 400 „ 500 | „ |
| 151 „ 152 | „ „ | „ 500 „ 600 | „ |
| 91 „ 92 | „ „ | „ 600 „ 700 | „ |
| 76 „ 77 | „ „ | above 700 | „ |

Since this one example will suffice to give a clear representation of the nature of the law, I shall limit myself to giving only the mean values of the molecular speeds for other gases and vapours, and these I shall tabulate together with the values of the specific gravity which have been used in their calculation. I have in this case not referred the density $\rho$ of a gas to that of water as unity, but instead of this I have introduced, as in § 13, the specific gravity $s$ referred to atmospheric air. This is a procedure which would not be admissible for exact scientific calculations, since atmospheric air is, as Jolly[1] has shown, by no means always of the same composition. Still, for the purpose in hand, this inexact procedure is justified by there being a still greater uncertainty in the values by reason of the deviations of the gases from Boyle's law. It is on this account that most observers have referred their numerical values to air; it would have served no purpose to reckon them with respect to water. The references appended to the table relate to the determinations of the specific gravities.

*Values at 0° C.*

| | Gas | $s$ | $G$ | $\Omega$ |
|---|---|---|---|---|
| 1 | Hydrogen . . . . . | 0·06958 | 1838 | 1694 |
| 2 | Marsh gas . . . . . | 0·555 | 636 | 600 |
| 3 | Ammonia . . . . . | 0·5967 | 628 | 579 |
| 4 | Water vapour . . . . . | 0·6235 | 614 | 566 |

1. Calculated from Lord Rayleigh's observations, 'Proc. Roy. Soc.' xxiii. 1888, p. 356.
2. Th. Thomson, 'Ann. of Phil.' i. 1813, p. 178.
3. Biot and Arago, 'Mém. de l'Inst.' vii. 1806, p. 320.
4. Gay-Lussac, 'Ann. Chim. Phys.' [2] i. 1816, p. 218; ii. p. 135.

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[1] *Abh. d. Akad. zu München*, xiii.; *Wied. Ann.* vi. 1879.

| | Gas | $s$ | $G$ | $\Omega$ |
|---|---|---|---|---|
| 5 | Hydrogen cyanide . . . . | 0·9476 | 498 | 459 |
| 6 | Carbon monoxide . . . . | 0·9678 | 493 | 454 |
| 7 | Nitrogen . . . . . . | 0·9726 | 492 | 453 |
| 8 | Ethylene . . . . . | 0·9745 | 491 | 453 |
| 9 | Atmospheric air . . . . | 1 | 485 | 447 |
| 10 | Nitric oxide . . . . . | 1·0388 | 476 | 438 |
| 11 | Oxygen . . . . . . | 1·1052 | 461 | 425 |
| 12 | Methyl alcohol . . . . | 1·120 | 458 | 422 |
| 13 | Hydrogen phosphide . . | 1·15 | 452 | 417 |
| 14 | Hydrogen sulphide . . . | 1·1912 | 444 | 409 |
| 15 | Hydrogen chloride . . . | 1·2474 | 434 | 400 |
| 16 | Nitrous oxide . . . . . | 1·5204 | 393 | 362 |
| 17 | Carbon dioxide . . . . | 1·5290 | 392 | 361 |
| 18 | Alcohol . . . . . . | 1·6133 | 382 | 352 |
| 19 | Methyl ether . . . . . | 1·617 | 381 | 351 |
| 20 | Methyl chloride . . . . | 1·763 | 365 | 337 |
| 21 | Cyanogen . . . . . | 1·8064 | 361 | 333 |
| 22 | Aceton . . . . . . | 2 | 343 | 316 |
| 23 | Ethyl chloride . . . . | 2·219 | 326 | 300 |
| 24 | Sulphur dioxide . . . . | 2·247 | 324 | 298 |
| 25 | Chlorine . . . . . . | 2·4502 | 310 | 286 |
| 26 | Ether . . . . . . | 2·586 | 302 | 278 |
| 27 | Arseniuretted hydrogen . . | 2·695 | 295 | 272 |
| 28 | Hydrogen iodide . . . . | 4·443 | 230 | 212 |
| 29 | Bromine . . . . . . | 5·5243 | 206 | 190 |
| 30 | Mercury . . . . . . | 6·976 | 184 | 169 |
| 31 | Iodine . . . . . . | 8·716 | 164 | 151 |

5. Gay-Lussac, 'Ann. Chim. Phys.' [1] xcv. 1815, p. 150.
6. Wrede, 'Berzelius Jahresbericht,' No. 22 for 1841, p. 72.
7. Calculated from Jolly, 'Wied. Ann.' vi. 1879, p. 536.
8. Th. Thomson, 'Mem. of the Wernerian Nat. Hist. Soc.' i. 1811, p. 516.
10. Bérard, 'Mém. de la Soc. d'Arcueil,' ii. 1809, p. 252.
11. Calculated from Jolly, 'Wied. Ann.' vi. 1879, p. 536.
12. Dumas and Peligot, 'Ann. Chim. Phys.' [2] lviii. 1835, p. 11.
13. H. Rose, 'Pogg. Ann.' xxiv. 1832, p. 121.
14. Gay-Lussac and Thénard, 'Rech. Phys. Chim.' i. 1811, p. 191.
15. Biot and Arago, 'Biot's Traité de Phys.' i. 1816, p. 383.
16. Colin, 'Ann. Chim. Phys.' [2] i. 1816, p. 218.
17. Regnault, 'Mém. de l'Acad.' xxi. 1847, p. 146.
18. Gay-Lussac, 'Ann. Chim. Phys.' [2] i. 1816, p. 218.
19. Dumas and Peligot, 'Ann. Chim. Phys.' [2] lviii. 1835, p. 21.
20. Bunsen, 'Ann. Chem. Phys.' xlvi. 1843, p. 33.
21. Gay-Lussac, 'Ann. Chim. Phys.' [1] xcv. 1815, p. 177.
22. Dumas, 'Ann. Chim. Phys.' [2] xlix. 1832, p. 209.
23. Thénard, 'Mém. de la Soc. d'Arcueil,' i. 1807, p. 121; 'Ann. Chim. Phys.' [1] lxi. 1807, p. 294.
24. Berzelius, 'Afhandl.' pt. 4; 'Schweigger's Journ.' xxiii. 1818, p. 116.
25. E. Ludwig, 'Ber. d. d. chem. Ges.' i. 1868, p. 232.
26. Gay-Lussac, 'Ann. Chim. Phys.' [2] i. 1816, p. 218.
27. Dumas, 'Ann. Chim. Phys.' [2] xxxiii. 1826, p. 358.
28. Gay-Lussac, 'Ann. Chim. Phys.' [1] xci. 1814, p. 16.
29. H. Jahn, 'Wiener Sitzungsber.' lxxxv. 1882, p. 778.
30. Dumas, 'Ann. Chim. Phys.' [2] xxxiii. 1826, p. 351.
31. Dumas, *ibid.* p. 346.

I could with little trouble have enlarged this table very considerably, since the tables of densities very carefully compiled by Poggendorff,[1] as well as the fuller tables of Boedeker[2] and those prepared by Traube,[3] would have furnished ample materials. But I fear that I have already included rather too much than too little in the above table.

For the calculated numbers can claim exactness only for those bodies to which the theory may be applied without hesitation, and thus, strictly speaking, only to gases which conform to Boyle's law. But a series of gases and vapours have been introduced into the table which do not obey this law, at least at the temperature 0° for which the calculations have been made; some, indeed, cannot exist in the gaseous state at 0°. For these bodies the calculated numbers possess no directly real meaning, but they may be used to calculate the real values of the molecular speed at a higher temperature $\vartheta$, at which Boyle's law does hold, by simple multiplication by the factor $\sqrt{(1 + a\vartheta)}$, where $a = 0{\cdot}00367$ (see § 14). Instead of making the calculation for these higher temperatures, which would have had to be different for different bodies, I have preferred to refer all numbers to one and the same temperature, so as to make them comparable with each other.

## 29. Equality of Temperature of Different Gases

Just as in a simple gas which is in equilibrium and at rest with respect to external bodies the state of motion of the molecules is subject to a definite law of distribution of speeds, so the distribution of energy in a mixture of two or more gases must also be equalised among the different kinds of molecules in a way regulated by law.

The law which regulates this more general case was also discovered by Maxwell, and a strict proof of it was given by Boltzmann. The calculation[4] showed that it is the same law as that which was found for the special case of a simple gas. *Maxwell's law of distribution is applicable equally to single and mixed gases.* There is, therefore, in gaseous mixtures, too, such a distribution of molecular energy that of all possible values of the kinetic energy a definite value can be assigned which will be found in any given particle more frequently than any other value, whether larger or smaller. The deviations from this most probable value of the molecular energy of motion follow the same law in each kind of molecules that are mixed in the gas. A definite amount of energy of forward motion occurs, therefore, in a particle of one kind with the same degree of probability as in a particle of another kind.

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[1] *Pogg. Ann.* xlix. 1840, p. 424.

[2] Boedeker, *Die gesetzmässigen Beziehungen zwischen der Dichtigkeit, der specifischen Wärme und der Zusammensetzung der Gase,* Göttingen 1857.

[3] Landolt and Börnstein's Tables, 1894, 2nd ed.

[4] See § 20* of the Mathematical Appendices.

From this follows directly a proposition first given by Clausius, that *in a mixture of two or more gases the molecules of both kinds possess on the average equal kinetic energy*; or, to express this by a formula, if $m_1$, $m_2$ are the molecular masses of the two gases, $G_1$, $G_2$ the mean values of the corresponding speeds as calculated from the values of the energy, then

$$\tfrac{1}{2}m_1 G_1{}^2 = \tfrac{1}{2}m_2 G_2{}^2\,;$$

or, if the arithmetic mean speed $\Omega$ be introduced instead of the magnitude $G$,

$$\tfrac{3}{16}\pi m_1 \Omega_1{}^2 = \tfrac{3}{16}\pi m_2 \Omega_2{}^2.$$

This mathematical proposition possesses an important physical meaning, which will be easily understood on recalling our former considerations (§§ 9, 14) regarding the increment of pressure with temperature. We there saw that the kinetic energy of the molecular motion forms the mechanical measure of temperature. If we further remember that two gases must attain equal temperatures when mixed together, the conclusion follows that *the equality of the temperature of two gases consists in equality of the mean energy of the forward motion of their molecules.*

These conclusions cannot be strictly proved without mathematical investigation into molecular mechanics. Still, we can show their probability without mathematical means if we consider the gases, not as already mixed, but as initially separated. And here we employ a law that is the result of experiment, viz. that if two gases of the same temperature are mixed with each other, the temperature remains unchanged; and we make an assertion which is little likely to meet with opposition, viz. that if two gases whose molecules have the same mean value for the energy of their to-and-fro motion are mixed with each other, the mean energy of both kinds of molecules will remain unchanged. That the total amount of energy in the mixture remains unchanged follows from the law of the conservation of energy. An inequality of the mean energy on mixture could therefore only arise if one of the gases suffered diminution of its energy below the mean value in order to raise that of the other above that amount, which would be very improbable. This analogy would therefore justify us in assuming also for unmixed gases the proposition first laid down by Clausius,[1] that *two gases have the same temperature when the mean energy of rectilinear motion of the molecules is the same for both gases.*

It is not, perhaps, superfluous to observe that the law laid down for the state of a gaseous mixture applies only to the condition of equilibrium. Hence those cases are excluded in which the mixture of gases is accompanied by chemical reactions. The law of the equality of molecular energy need not therefore be applicable to such gaseous mixtures as chemically combine in a flame; even if the original two gases which combine in the flame possessed equal temperatures, it is still possible, and indeed probable, that the molecules of the products of combustion possess a far higher temperature and greater energy than the molecules of the primitive gases while uncombined, as Smithells[2] assumes. A thermometer which is held in a flame would then indicate, not the temperature of combustion, but the mean temperature of the burnt and unburnt gases existing in the flame.

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[1] *Pogg. Ann.* c. 1857, p. 370; *Abhandl.* 2. Abth. 1867, p. 247; transl. *Phil. Mag.* [4] xiv. 1857, p. 108.

[2] *Phil. Mag.* [5] xxxvii. 1894, p. 245.

## 30. Gay-Lussac's Law of Gaseous Densities

As simple consequences of the theorems of molecular mechanics that have been given, we deduce certain laws of theoretical chemistry, of which the law of gaseous densities obtained empirically by Gay-Lussac[1] should first be mentioned.

Two gases are at the same temperature when the mean kinetic energies of a molecule of each,

$$E_1 = \tfrac{1}{2}m_1 G_1^2 \text{ and } E_2 = \tfrac{1}{2}m_2 G_2^2,$$

are equal to each other. By § 16 they exert equal pressures when their kinetic energies per unit volume,

$$K_1 = \tfrac{1}{2}\rho_1 G_1^2 \text{ and } K_2 = \tfrac{1}{2}\rho_2 G_2^2,$$

are equal to each other. Hence it follows that, *if two gases are not only at the same temperature, but also under the same pressure, their densities must be in the ratio of their molecular masses*, or

$$\rho_1 : \rho_2 = m_1 : m_2.$$

This proposition deduced from our theory agrees substantially with Gay-Lussac's law, that the quantities of two gases which can chemically combine with each other occupy volumes which, when the measurements are made at the same temperature and under the same pressure, are either equal or in the ratio of simple integers. More simply expressed, this theorem runs—*the densities of two gases are in a simple ratio, expressed by integers, to their stoichiometric quantities.* If we denote the latter by $Q_1$, $Q_2$, and put $n_1$, $n_2$ to represent integers, Gay-Lussac's law gives

$$\rho_1 : \rho_2 = n_1 Q_1 : n_2 Q_2.$$

This empirical law agrees exactly with that deduced from theory *if the molecular masses $m$ of the gases are to their stoichiometric quantities $Q$ in ratios given by simple integers*, or

$$m_1 : m_2 = n_1 Q_1 : n_2 Q_2;$$

a condition which is obviously fulfilled if Dalton's atomic theory forms the true explanation of the constancy of the chemical equivalents, since a molecule can contain only an integral and not a fractional number of atoms.

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[1] *Mém. de la Soc. d'Arcueil*, ii. 1809, p. 207; *Gilb. Ann.* xxxvi. 1810, p. 6.

The relations considered above may be made useful in theoretical chemistry in two ways. We may either, with Gay-Lussac, calculate by means of the given proportion the unknown density of a gas or vapour from its chemical equivalent which has been determined from its chemical action; or, inversely, from its observed density we may deduce its chemical equivalent. For this purpose Avogadro's law, which is discussed in the next paragraph, is of service.

## 31. Avogadro's Law

The proportion deduced from Maxwell's theory, viz.

$$\rho_1 : \rho_2 = m_1 : m_2,$$

or the theorem that the densities $\rho_1$, $\rho_2$ of two gases at the same temperature and under the same pressure are in the ratio of their molecular masses $m_1$, $m_2$ in the gaseous state, is capable of a very simple interpretation, which is, therefore, the more important.

In the meaning assigned in § 13 to the idea of density, $\rho$ is nothing else than the mass of all the $N$ molecules contained in unit volume, or

$$\rho = Nm.$$

For two different gases we must write

$$\rho_1 = N_1 m_1 \text{ and } \rho_2 = N_2 m_2,$$

where the meaning of the symbols is plain. If we substitute these values of the densities in the above proportion we obtain the equation

$$N_1 = N_2,$$

which, expressed in words, gives the theorem that *two different gases, when they are at the same temperature and under the same pressure, contain equal numbers of molecules in equal volumes.*

This is called Avogadro's law, after its discoverer.

Although the considerations by which Avogadro[1] arrived at it are closely bound up with views which were then universally accepted, but are now rejected, viz. with the assumption of a material caloric, yet the experimental results from which he started, and the conclusions he founded on them, agree substantially with those which we have here employed. He relied especially on the law of Gay-Lussac, which was discussed in the last paragraph, and from which, even without this special theory of gases, Avogadro's law can be easily deduced with at least very great probability.

On this ground Clausius, who had already pointed out the significance of this law for theoretical chemistry in his first memoir[2] on the kinetic theory of gases, was able to proceed the reverse way. From the laws of Gay-Lussac and Avogadro he inferred the law, first given by him, that two gases have the same temperature when the mean kinetic energy of their molecular motion is the same, a law which, aided by Maxwell's later researches, we have deduced from the mechanics of molecules.

Avogadro's law forms one of the most important foundations of theoretical chemistry; for by its aid we are in a position to calculate the molecular mass of a substance from its density in the state of gas. For if in the formula

$$\rho = Nm$$

$N$ is a number which is the same for all gases and vapours, we can express the values of the molecular mass for all gases in terms of any arbitrary unit, such, for instance, as the molecular mass of hydrogen. The values of the molecular masses so found do not all agree with the atomic masses, but are in cases multiples of them. A molecule, therefore, must in general consist of several atoms, as we have already assumed to be possible.

Further inquiry into this interesting subject, which is more concerned with chemistry than with physics, I must here abandon, and all the more so as it has obtained a thorough treatment in a treatise by my brother.[1]

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[1] *Journ. de Phys. par Delamétherie*, lxxiii. 1811, p. 58; lxxviii. 1814, p. 131; *Mem. di Torino*, xxvi. 1821, p. 440.

[2] *Pogg. Ann.* c. 1857, p. 353; *Abhandl. über Wärmetheorie*, 2. Abth. 1867, p. 229; transl. *Phil. Mag.* [4] xiv. 1857, p. 108.

## 32. Coefficient of Expansion

From the relation found in § 16 between the temperature of a gas and the mean value of the kinetic energy of its molecules, follows another law which has in like manner been confirmed by experiment.

Since two gases have the same temperature $\vartheta$ when the mean values of the kinetic energy of their molecules are equal, *i.e.* when

$$\tfrac{1}{2}m_1 G_1^2 = \tfrac{1}{2}m_2 G_2^2,$$

the values also of their molecular energies are equal when they are both at the temperature 0°, or, in the notation already used in § 14,

$$\tfrac{1}{2}m_1 \mathfrak{G}_1^2 = \tfrac{1}{2}m_2 \mathfrak{G}_2^2.$$

But, if $\alpha_1, \alpha_2$ are the thermal expansibilities of the two gases,

$$G_1^2 = \mathfrak{G}_1^2(1+\alpha_1\vartheta),$$
$$G_2^2 = \mathfrak{G}_2^2(1+\alpha_2\vartheta).$$

From these four formulæ we obtain the equation

$$\alpha_1 = \alpha_2,$$

or the law that *the thermal expansibilities of all gases are the same.*

This law, which has been already mentioned in § 15, in the determination of the absolute zero of temperature, was empirically established by Gay-Lussac[2] and Dalton,[3] and still earlier, as the former tells us, by Charles. If it now appears as a logical deduction from the theory, we must see in this coincidence a weighty and convincing argument for the truth of the theoretical views from which we have started in explaining gaseous pressure.

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[1] Lothar Meyer, *Die modernen Theorien der Chemie*, 5. Aufl., Breslau 1884; 6. Aufl. I. 1895.

[2] *Ann. Chim. Phys.* xliii. 1802, p. 137; *Gilb. Ann.* xii. p. 257.

[3] *Mem. of the Manchester Lit. and Phil. Soc.* v. 1802, p. 595; *Gilb. Ann.* xii. p. 310.

### 33. Maxwell's Law for a Gas in Motion

In the simple form in which we have hitherto used it, Maxwell's law of distribution rests on the assumption that the gas is in equilibrium and at rest as a whole. Hitherto, we have always assumed that there is no other motion in the gas than the invisible to-and-fro motion of its particles. Beside this molecular motion, the effect of which we perceive only in the pressure and heat of the gas, there should be no directly perceptible motion, no flow, no rotation, no change of the volume occupied; there should, therefore, be no sort of cause for the centroid of the whole mass of gas to change its position, nor, indeed, for that of any portion of the gas of finite magnitude; only the single atoms were endowed with independent motions, which they executed without disturbing the equilibrium of the gas as a whole.

If we discard this assumption Maxwell's law must be modified, and the necessary modification in a special simple case is easy to see. If we impart to the whole mass of gas and its containing vessel a uniform motion of translation, there is no reason at all for any change in the to-and-fro motion of the molecules. Both motions, the molecular and the molar, will exist together without mutually disturbing each other. If we compound them by the known rule of the parallelogram of velocities, we get for each molecule the direction and magnitude of the velocity with which it moves when the gas as a whole is in translatory motion. Herewith, then, the law of distribution for this case is determined. It does not seem necessary to express here in mathematical formulæ[1] this more general law; for the more general law is easily to be deduced from Maxwell's known law of distribution. If we diminish, that is to say, the actual velocity of a molecule by the velocity of translation of the centroid of the gas as a whole, Maxwell's simple law for the probability of a definite speed again comes to view. It is obvious that the subtraction of the velocity of the centroid of the whole gas from that of a molecule amounts to bringing the principle of the parallelogram into play, or, what comes to the same thing, to subtracting the components of both velocities from each other.

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[1] See §§ 16*, 17* of the Mathematical Appendices.

The most general case can be at once deduced from this very simple one. If the gaseous mass so moves that the molar velocity is not everywhere the same, but in different places is different in magnitude and direction, we have at each particular place to subtract the velocity of flow at that place (which is the same thing as the molar velocity), and the remaining molecular motion will satisfy Maxwell's law.

## 34. Pressure of a Gas in Motion. Resistance

If such a distribution of molecular velocities exists, the different directions can no longer be looked upon as having no distinction. The pressure, too, of a streaming gas will, therefore, no longer be equally great in all directions. In the direction of the flow the velocity and pressure will be greater than in any other direction; the pressure is increased by the stress which the gas by its motion exerts on a surface in its way.

It is easy to calculate this increase of pressure if we remember that, according to the kinetic theory, the pressure consists in a transference of momentum. In a gas at rest this transference is effected by the to-and-fro motion of the molecules. In a gas in motion there is an additional cause in the velocity of flow by which not only momentum but also mass is transferred. Through a surface $F$ at right angles to the direction of flow there passes in unit time a volume $Fa$ and a mass $\rho Fa$, if $a$ denotes the velocity. This mass possesses the momentum

$$\rho F a^2.$$

In consequence of the flow, therefore, the momentum transferred in the direction of the flow increases in unit time by

$$\rho F a^2.$$

Since, now, according to our theory, the pressure is measured by the momentum which is transferred in unit time across unit area, we must conclude that the pressure exerted by the gas in the direction of its motion is greater than $p$ by $\rho a^2$ in consequence of the flow, and so rises to

$$p + \rho a^2 = \rho(\tfrac{1}{3}\pi\Omega^2 + a^2).$$

This increment of the pressure in the direction of the flow makes itself perceptible as *stress* when a surface is put in the way of the flowing stream of gas.

An equally great stress results between the surface and the gas when the gas is at rest and the surface is moved with velocity $a$ against the gas in the direction of its normal. The force which then results and tends to stop the motion is felt as resistance, and the *resistance of a gas* is therefore also determined by the formula

$$\rho F a^2,$$

which expresses the law that the resistance increases proportionally to the square of the velocity.

That this law holds not only for the resistance in a liquid, but also for the motion of a body in air, has already been proved by Newton and Hawksbee[1] by means of experiments on falling bodies; it has lately been found also for other gases by Cailletet and Colardeau[2] by means of observations on the gases in flow. A remarkable confirmation of the formula deduced for gaseous resistance arises from an observation made by Hirn,[3] from which too Hirn himself thought he must conclude that the kinetic theory of gases is wrong. He found in fact that the resistance does not alter with the temperature if the density is kept unchanged. With this fact the theoretical formula is in perfect agreement, as it does not contain the molecular velocity $G$, but only that of the flow $a$.

The range of applicability of Newton's formula is however dependent on definite limits for the value of the velocity $a$. If this value is too great, the resulting heat (see § 19) cannot be disregarded; if it is too small, the viscosity of the air (see Chapter VII.) cannot be left out of account.

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[1] Newton, *Principia*, bk. ii. prop. 40; Hawksbee, *Physico-mechan. Experiments*, London 1709; Musschenbroek, *Tentamina Exper. in Acad. del Cimento*, Lugd. 1731, pt. ii. p. 118.

[2] *Comptes rendus*, cxvii. 1893, p. 145.

[3] *Mém. de l'Acad. de Belgique*, xiii. 1882.

In another relation, too, the formula for the resistance

$$\rho F a^2$$

does not exactly correspond to the results of experiment. Hutton[1] and Borda[2] long ago found that the resistance is not exactly proportional to the extent of the surface $F$ of the moved body, and that it depends also on the curvature of the surface. For plane discs which move at right angles to their plane, Schellbach,[3] G. Hagen,[4] and Hirn[5] have shown that the factor $F$ would be more exactly replaced by expressions of the form

$$AF^n \quad \text{or} \quad AF(1 + Bq),$$

where $A$, $B$ are constants, $n$ an exponent greater than 1, and $q$ the circumference of the disc. The cause of this deviation is easy to indicate. Part of the air which is pushed in front of the disc turns off sideways, and the resistance is thereby diminished; the theoretical expression has therefore to be multiplied by a proper fraction $A$. This fraction, however, depends also on the size of the disc, since the air cannot slide aside so easily in front of a large surface as in front of a smaller; hence the value of the fraction increases with the area $F$ or with the circumference $q$ of the disc.

## 35. Reaction. Cross-pressure

In a flowing gas there is also, in the direction opposite that of the flow, a change of pressure due to the flow, which is also an increase and not a decrease. To prove this statement I might merely rely on the mechanical principle that action and reaction, and consequently pressure and counter-pressure, must be always equal. Yet I prefer to repeat a proof which has been given by Clausius,[1] by which also the rise of pressure already described in the direction of the flow is better explained.

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[1] *Trans. Roy. Soc. Edin.* ii. 1790.

[2] *Mém.* Paris 1763, 1767.

[3] *Pogg. Ann.* cxliii. 1871, p. 1.

[4] *Ibid.* clii. 1872, p. 95.

[5] *Mém. de l'Acad. de Belgique*, xiii. 1882.

For this we start, as in the consideration (§ 12) of the state of equilibrium, from Joule's assumption,[2] which even in this case is admissible, that the pressure caused by the motion of the gaseous molecules so operates as if a third part of the molecules move to and fro along the normal to a stressed surface, while the other two-thirds move parallel to this surface. Of the first third one-half will at every moment have a molecular velocity $G$ in the same direction as the velocity of flow $a$, while the other half has a molecular velocity in the opposite direction. Therefore, of the $N$ molecules contained in unit volume, $\frac{1}{6}N$ move with a resultant velocity $G + a$ in the direction of the flow, and simultaneously the same number $\frac{1}{6}N$ move in the opposite direction with the resultant velocity $G - a$.

The difference $G - a$ we may take to be positive, since the mean molecular velocity $G$ is very great, while the observed speeds of flow are for the most part considerably less. The greatest velocity which the wind attains—that, for instance, of the most fearful storm—may be taken at about only one-tenth of that with which the molecules move about. But if, indeed, it should happen that $a$ were greater than $G$, the argument would not be invalidated.

If, now, one-sixth of all the molecules move with the velocity $G + a$ in the line of flow, the number which pass through a surface $F$ in unit time in this direction is

$$\tfrac{1}{6}NF(G + a),$$

and they carry with them momentum equal to

$$\tfrac{1}{6}NmF(G + a)^2.$$

In the backward direction there pass

$$\tfrac{1}{6}NF(G - a)$$

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[1] *Bulletin de l'Acad. de Belgique* [3] xi. 1886, p. 180; *Mech. Wärmetheorie*, 2. Aufl. iii. p. 248.

[2] The calculation is carried out independently of this assumption, and purely on the basis of Maxwell's law, in §§ 7* and 43* of the Mathematical Appendices.

molecules through the surface $F$ in unit time, and these carry back the oppositely directed momentum

$$\tfrac{1}{6}NmF(G - a)^2.$$

The two halves into which the gaseous mass is separated by the surface $F$, therefore, both gain and lose momentum, and the question is, What variation in the law of distribution results? If we call that side the right towards which the flow is directed, we can say that the right side gains an amount of momentum directed towards the right which is equal to

$$\tfrac{1}{6}NmF(G + a)^2,$$

while it loses momentum directed towards the left equal to

$$\tfrac{1}{6}NmF(G - a)^2.$$

The right half thereby obtains an amount of right-directed momentum which exceeds the left-directed momentum, and this excess is equal to

$$\tfrac{1}{6}NmF\{(G + a)^2 + (G - a)^2\}.$$

The excess of left-directed over right-directed momentum which arises in the left half is of equal amount; for this half gains left-directed momentum equal to

$$\tfrac{1}{6}NmF(G - a)^2,$$

and loses right-directed momentum equal to

$$\tfrac{1}{6}NmF(G + a)^2,$$

so that the left-directed momentum in the left half will exceed the right-directed momentum in the left half by the amount

$$\tfrac{1}{6}NmF\{(G - a)^2 + (G + a)^2\}.$$

These formulæ, however, do not account for the whole changes that occur. In the case of a flowing gas the other two-thirds of the molecules come also into account; for these, too, take part in the flow, and therefore possess the velocity $a$ in the direction perpendicular to the surface $F$. In this direction, therefore, there pass

$$\tfrac{2}{3}NFa$$

molecules from the left half to the right in the unit of time, and these carry with them the momentum

$$\tfrac{2}{3}NmFa^2.$$

The total excess, therefore, of right-directed over left-directed momentum which is produced in unit time in the right half is given by

$$\tfrac{1}{6}NmF\{(G+a)^2+(G-a)^2\}+\tfrac{2}{3}NmFa^2$$
$$=NmF(\tfrac{1}{3}G^2+a^2).$$

Just as large is the excess of left-directed over right-directed momentum which occurs in the left half in unit time; for the former increases by

$$\tfrac{1}{6}NmF(G-a)^2,$$

while the latter diminishes by

$$\tfrac{1}{6}NmF(G+a)^2+\tfrac{2}{3}NmFa^2.$$

Now, according to the kinetic theory of gases, the pressure is nothing else than the momentum carried across unit area in unit time; consequently the pressure is expressed by the formula

$$p=Nm(\tfrac{1}{3}G^2+a^2),$$

and this formula holds good equally well for the direction in which the gas flows and for the opposite direction. As for the former direction, the added term

$$Nma^2=\rho a^2$$

expresses the stress exerted by the stream, so for the opposite direction it represents the equal reaction-stress which is exerted by the flowing gas on the containing vessel.

For a direction at right angles to the stream the pressure will be expressed by the formula

$$p=\tfrac{1}{3}NmG^2,$$

which holds good for all directions in a gas at rest. An essential difference, however, consists in the magnitude $G$ not having the same value for a flowing gas as it has in a gas at rest. This is, at least, the case when the gas is not brought into a state of motion by the application of energy from without, but is forced by its own pressure to rush along an opened pipe. In this case the amount of energy of the mass of gas remains unaltered. If, then, the gas were under the pressure

$$p_0 = \tfrac{1}{3}\rho G_0^2$$

when at rest, and its kinetic energy per unit volume were therefore

$$K_0 = \tfrac{1}{2}\rho G_0^2$$

before the flow began, the whole energy of molecular motion and flow in the exit pipe, viz.

$$K = \tfrac{1}{2}\rho G^2 + \tfrac{1}{2}\rho a^2,$$

must be the same as before. We have, therefore,

$$G^2 = G_0^2 - a^2,$$

or the molecular speed $G$ of the flowing gas is less than the molecular speed $G_0$ of the gas at rest. The *cross-pressure*

$$p = \tfrac{1}{3}\rho G^2$$

of the gas when flowing is, therefore, less than the pressure when the gas was at rest. This lowering of the pressure by the flow depends, as the formulæ show, on cooling being produced.

Since these formulæ contain the velocity only in its square, they are independent of the direction of the motion, and hold, therefore, as well for to-and-fro oscillations as for the propagation of the longitudinal waves of sound. On this depend the apparent attractions and repulsions in air when sounding and in the ribbed dust-figures of Kundt.[1]

## 36. Propagation of Sound

When we develop the theory of sound according to the kinetic hypothesis we have also to consider two sorts of motion which exist without disturbing each other. In addition to the molecular motion which is present even in a gas at rest there are the to-and-fro motions which constitute the vibrations of sound. The latter motions spread from one place to another, and the cause of this transmission is the molecular motions which bring the particles that execute the sound-vibrations into contact with others. From this it follows that the velocity of propagation of sound cannot depend on the nature of the sound-vibrations, but only on the molecular motions.

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[1] See W. König, *Wied. Ann.* xlii. 1891, p. 353; *Zeitschr. f. phys. u. chem. Unterr.* 8. Jahrg. 1895, p. 191.

If we paid no regard to the variations in temperature which a gas undergoes by condensation or rarefaction, it would be easy to answer the question as to the speed with which, on the basis of the assumptions of the kinetic theory, a sound wave is propagated. If sound consists in alternate rarefactions and condensations of the air, the speed of its propagation cannot be different from the speed with which any inequality of the pressure that arises at any place would spread through air-filled space.[1] Now, according to our theory the pressure arises from the to-and-fro motions of the particles, and is exerted and carried on from one layer to another by the same cause; the velocity with which a pressure- or sound-wave is propagated must therefore be just as great as that with which the particles of gas move to and fro in the direction of propagation of the wave. The value of the component of the molecular motion in the given direction, and not the resultant velocity of the particles, comes therefore into account in the calculation of the velocity of sound; and hence it follows at once that *the speed of propagation of sound in a gas must be smaller than the mean speed of the molecular motion in this gas.* This theoretically deduced proposition is completely confirmed by experiment; for instance, in atmospheric air at 0° C. the speed of sound is about 332 metres per second, and is consequently considerably less than the mean molecular speeds $G = 485$ and $\Omega = 447$ (§ 28).

How much smaller the speed of sound is we may easily, and with sufficient exactness, determine in the same way as in § 10 we calculated the pressure of a gas.[2] If the energy of the motion of the molecules in a given direction is one-third part of the whole energy, we might look on the magnitude

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[1] This conclusion has been experimentally confirmed by Calderoni, *Wied. Beibl.* iii. p. 155.

[2] More mathematically strict calculations have been made by Stefan (*Pogg.*

$$G\sqrt{\tfrac{1}{3}}$$

as the mean value of the component in a given direction, $G$ being, as before, the mean molecular speed; for, as the energy varies as the square of the velocity, the velocity varies as the square root of the energy. We therefore find for the velocity $v$ of sound the formula

$$v = G\sqrt{\tfrac{1}{3}},$$

which shows that $v$ is less than $G$; we also have

$$v = \Omega\sqrt{\frac{\pi}{8}},$$

from which it appears that Maxwell's mean value $\Omega$ of the molecular speed is also greater than that of sound.

If we put these formulæ into the form

$$v^2 = \tfrac{1}{3}G^2 = \tfrac{1}{8}\pi\Omega^2 = p/\rho$$

we obtain Newton's[1] formula, with which the speed of sound can be calculated from the pressure $p$ and the corresponding density $\rho$ of the gas.

But, as Laplace[2] first saw, this formula needs a correction. The oscillations constituting sound depend not so much on the actual pressure and density of the gas as on the changes which they simultaneously undergo in consequence of the alternate condensations and rarefactions. With more correctness, therefore, should we have expressed $v$ in terms of the variations which $p$ and $\rho$ undergo instead of in terms of $p$ and $\rho$ themselves, and this could have been

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Ann. cxviii. 1863, p. 494), Roiti (*Mem. dell' Accad. dei Lincei* [3] i. 1876, pp. 9, 762; *Nuovo Cimento* [2] xvi. 1876; [3] i. 1877, p. 42), and Brusotti (*Mem. Scient. del Ist. Tecnico di Pavia*, 1874–5, p. 171); further by oorweg (*Arch. Néerl.* xi. 1876, p. 131; *Pogg. Beiblätter*, i. 1877, p. 209), es and H. A. Lorentz (*Versl. en Med. K. Akad. Amst.* xv. 1880), hlemüller (*Die Fortpflanzungsgeschw. in einem theor. Gase, bearb. auf Grund d. dyn. Gastheorie*, Prag 1894). S. T. Preston has given an elementary explanation of the process in *Phil. Mag.* [5] iii. 1877, p. 441.

[1] *Principia*, ii. § 8, prop. 49, probl. 11.

[2] *Ann. Chim. Phys.* [2] iii. 1816, p. 238; xx. 1822, p. 266; *Méc. Cél.* v.

done equally easily. For by Boyle's law, if $p + dp$ and $\rho + d\rho$ represent the values of $p$ and $\rho$ when increased by compression, the ratio

$$\frac{p}{\rho} = \frac{p + dp}{\rho + d\rho} = \frac{dp}{d\rho}$$

is constant so long as the temperature remains unchanged. We might therefore have written

$$v^2 = \frac{dp}{d\rho}$$

for the formula giving the speed of sound; and herein the increment $dp$ of pressure and the corresponding increment $d\rho$ of density may be taken either as finite or as infinitely small magnitudes.

But the ratio of the pressure to the density remains constant only so long as the temperature of the gas remains unaltered. If, however, a gas is made to occupy a smaller volume, not only do the pressure and density increase, but also the temperature; and if the gas expands, not only do its pressure and density diminish, but its temperature falls too. This rise and fall of temperature, when the volume undergoes change, have both the effect of causing the pressure to alter in greater measure than the density, and therefore the ratio of $dp$ to $d\rho$ has in the actual case a greater value than Boyle's law gives it when the temperature is not taken into account. Thus the formula must be completed by a factor which is greater than 1, and, according to the equations of the theory of heat, which have been established by Laplace and others, this factor is the ratio of the specific heat $C$ at constant pressure to the specific heat $c$ at constant volume. Consequently we have

$$v^2 = \frac{C}{c}\frac{p}{\rho} = \tfrac{1}{3}\frac{C}{c}G^2 = \frac{\pi}{8}\frac{C}{c}\Omega^2,$$

and the speed of sound itself is given by

$$v = \Omega\sqrt{(\pi C/8c)}.$$

That with this improved formula, also, the ratio of $v$ to $\Omega$ is less than 1, I will show by taking atmospheric air as an example. Putting for this substance

$$C = 1{\cdot}405\, c,$$

as is deduced from the observations that are discussed in detail in § 55, we obtain

$$v = 0{\cdot}74\,\Omega,$$

and, on substituting for $\Omega$ its value 447, as given in § 28,

$$v = 332 \text{ metres per second.}$$

The ratio 0·74 calculated for air holds good equally for the other so-called permanent gases, and is also approximately admissible for those that are condensable, so that in general we may assume the ratio of the speed of sound to the mean molecular speed to be about $\frac{3}{4}$ in round numbers.

According to the formula, the speed $v$ of sound must decrease with falling temperature, just as the molecular speed $\Omega$. This theoretical conclusion is confirmed by experiment.[1] According to experiments made by Greely[2] in Arctic regions, at temperatures between − 8° and − 48° C., the speed decreases by 0·603 metres per second with every degree; its value, therefore, may be represented as a function of the temperature $\vartheta$ by the formula

$$\begin{aligned} v &= 332 + 0{\cdot}603\,\vartheta \\ &= 332\,(1 + 0{\cdot}00182\,\vartheta), \end{aligned}$$

while the molecular speed is given by the formula

$$\begin{aligned} \Omega &= 447\sqrt{(1 + 0{\cdot}00367\,\vartheta)} \\ &= 447\,(1 + 0{\cdot}00183\,\vartheta), \end{aligned}$$

when $\vartheta$ is small enough.

## 37. Effusion of Gases

One directly valuable result of the numerical calculation of the mean speed with which the molecules of different gases move is obtained from the fact that from these numbers we can at once infer the speed with which gases will issue through fine openings in a thin wall. We have, therefore, to consider the phenomenon designated *effusion* by Thos. Graham, for which also the name *diffusion* has been used, thus giving rise to mistakes.

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[1] Benzenberg, *Gilb. Ann.* xlii. 1812, p. 1.

[2] *Meteorolog. Zeitschrift*, 7. Jahrg. 1890, p. 6 (25. Jahrg. d. *Zeitschr. d. öst. Ges. für Met.*).

The theory of this process has been already developed by Daniel Bernoulli,[1] and its exactness has been confirmed by the experiments of Graham[2] and Bunsen.[3]

Bernoulli rests his theory on a proof of the proposition that Torricelli's theorem is not only applicable to the efflux of liquids, but may be extended also to gases. From this it at once follows that the speed of efflux is proportional to the square root of the pressure. Since, according to the kinetic theory, the pressure varies as the square of the mean speed, the signification of Torricelli's theorem on the kinetic hypothesis is that the speed of efflux of a gas is proportional to the mean molecular speed of its molecules.

We should have been able to arrive directly at this conclusion from the assumptions of the theory of gases, even without employing Torricelli's theorem; for it is clear that one of the to-and-fro moving particles which reaches the orifice can issue through it with no other speed than that which it possessed before. The speed of efflux thus originates directly from the speed of the molecular motion, and the mean speed of the issuing particles must therefore be simply proportional to the mean molecular speed.

Here again, therefore, appears the same ratio which we noted in the investigation on the speed of sound. The speed of efflux, equally with the speed of propagation of sound, is proportional to the mean molecular speed. The reason for this simple relation between effusion and the motion of sound is not far to seek. In both processes we are concerned with the propagation of differences of pressure. In the motion of sound periodical alternations of condensation and rarefaction of the air are transmitted; in efflux the pressure goes from the compression vessel into outer space. The difference consists only in this, that in the case of sound the pressure alone is transmitted, whereas in effusion the transmission of pressure can only be effected by the gas itself flowing from the compression vessel into space of lower pressure, and thereby raising the density in this outer space. Energy and mass therefore flow out together with equal speed, and the gas would flow out with the speed of sound if there were no obstacle in the way.

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[1] *Hydrodynamica*, Argentorati 1738, sect. 10, § 34, p. 224.

[2] *Trans. Roy. Soc. Edin.* xii. 1834, p. 222; *Phil. Mag.* ii. 1833, p. 175; *Pogg. Ann.* xxviii. 1833, p. 331; *Phil. Trans.* 1846, p. 573; 1863, p. 385.

[3] *Gasometrische Methoden*, Braunschweig 1857, pp. 128, &c.; 2nd ed. 1877, pp. 185, &c.

This assumption, however, is untenable, for on the one hand the friction which the gas experiences from the rim of the orifice retards it, and on the other the pressure in the space into which it flows acts as a resistance.

The first disturbance, that by friction, is avoided as much as possible by making the orifice small and using a thin wall. For if the wall is not very thin the orifice acts as a tube in which the flow would be considerably diminished by the internal friction of the gas. And the orifice must be small, as otherwise it would offer room for eddies and vortices to form which would hinder the regularity of the efflux; for the turbulent motions that must occur in wider orifices would cause heating effects which would consume a large part of the energy present.

The other disturbance, that by the back pressure of the space into which the efflux occurs, is removed when the gas flows into vacuous space. In this case the issuing mass of gas appears to be almost exactly proportional to the pressure which drives it out, as was *à priori* to be expected. ? Since the density of a gas is proportional to its pressure, we must from this experimental result draw the conclusion that the speed with which a gas flows into vacuous space is independent of the pressure which causes the flow. But in this conclusion lies a confirmation of the inference already drawn from the theory, viz. that the speed of efflux of a gas is determined only by the speed with which sound travels in this gas, or, what amounts to the same thing, on the mean speed of molecular motion in the gas.

The manner of dependence of the speed of efflux on that of the molecular motion could be assigned if we knew how many molecules issue per unit of time, and what is the pressure in the orifice itself. The former question may be easily answered if we are content with an approximation which must be admissible when the excess of pressure and, therefore, the speed of efflux are small. With this assumption we can make the calculation just as for a gas at rest. We need only determine the number of molecules which are forced per unit time out of the interior of the vessel into the orifice. To simplify the calculation we shall further provisionally assume that all the particles move with the same mean speed $\Omega$.

Before we determine the number of particles which arrive at the orifice, let us find the number of those which reach it in a given direction. In the accompanying diagram

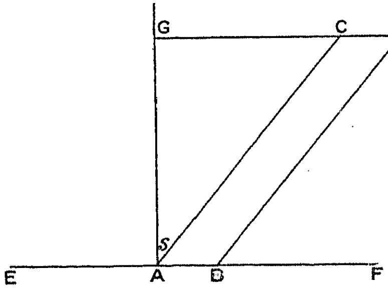

FIG. 3

let $EF$ denote the wall of the containing chamber, and $AB$ the orifice in the wall. Let $CA$ be the direction corresponding to the number of particles we are considering, and let it make angle $s$ with the normal $AG$. We see at once from the diagram that all particles which can meet the surface $AB$ in the given direction must come from a volume $CABD$, the edges $CA$, $DB$ of which are parallel to each other. If we wish to determine the number of particles that pass through $AB$ in unit of time, we have to limit the space $CABD$ by taking the lengths $CA$, $DB$ to measure the speed $\Omega$. For it is obvious that the surface $AB$ can be reached in unit time only by such particles as were initially distant from $AB$ by a less length than the path $\Omega$ traversed in unit of time. The volume $CABD$, from which the molecules come, is equal to

$$GA.AB = F\Omega \cos s,$$

where $F$ denotes the area of the orifice $AB$, and $\Omega \cos s$ is put for $GA$; and the number of molecules we denote by

$$nF\Omega \cos s.$$

We have still the number $n$ to determine. It represents the number of particles which move in unit volume in the direction given by $CA$ and therefore determined by $s$. This number is easy to calculate for a gas at rest, since in this case no one direction differs from any other, equal numbers of molecules therefore moving in every direction. Consider all the $N$ particles which are in the unit volume to be brought to one and the same point $A$, and to begin their rectilinear paths from this point; then at a small area $K$ of a sphere described about $A$ with unit radius there will arrive

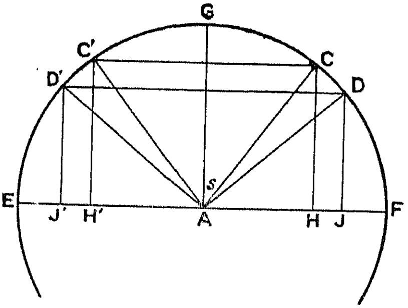

FIG. 4

$$\frac{K}{4\pi}N$$

particles; for the whole sphere, whose area is $4\pi$, will be symmetrically met by the $N$ particles. If we take the element $K$ to be the zone $CDD'C'$ obtained by rotating the radii $AC$, $AD$ about the normal $AG$ as axis, then

$$K = 2\pi r\Delta,$$

if we denote by $\Delta$ the breadth $CD = C'D'$ of the zone, and by $r$ the mean radius of the circles which make up this zone and are parallel to its boundaries $CC'$ and $DD'$. The number, therefore, of particles which meet this zone is

$$\frac{1}{4\pi}KN = \tfrac{1}{2}\Delta Nr.$$

We may look on this expression as being the value of $n$ when we take the angle $CAG$ of the same value $s$ as in the former figure. For the number which we have found for the particles which fly out from $A$ in a given direction is just as great as that which we are seeking, viz. the number which reach $A$ in the opposite direction. In this respect only do we alter and extend the meaning of $n$, that we count not only the particles which move in a given direction in space, but include also all those whose directions form the same angle with the normal $AG$.

If we put this value

$$n = \tfrac{1}{2}\Delta Nr$$

into the above formula we obtain the number of all the particles which in unit time meet the area $F$ at an inclination $s$, which is therefore

$$\tfrac{1}{2}NF\Omega r\Delta \cos s.$$

This expression may be simplified by our replacing $\Delta \cos s$, which represents the projection of the breadth $CD = \Delta$ of the zone on the plane $EAF$, by the line $HJ = H'J' = \delta$; this gives

$$\tfrac{1}{2}NF\Omega r\delta$$

for the number of particles which in unit time meet the area $F$ from the zone $CDD'C'$.

From this we obtain the whole number of the particles which arrive at the area $F$ in the unit time by summing the expression for all the zones, *i.e.* by evaluating the magnitude

$$\tfrac{1}{2}NF\Omega\ \Sigma.r\delta.$$

To calculate the sum $\Sigma.r\delta$, let us take the zones so as all to have the same value $\delta$; we therefore divide the line $AF$, whose length is 1, into $q$ equal parts (where $q$ is a very large number), and put

$$HJ = \delta = \frac{1}{q}.$$

Then, taking the radius $r$ as the arithmetic mean of the bounding radii $AH$ and $AJ$ of the zone, or

$$r = \tfrac{1}{2}(AH + AJ),$$

we can express it as a multiple of $\delta$; for if

$$AH = (\nu - 1)\delta \quad \text{and} \quad AJ = \nu\delta,$$

where $\nu$ is an integer lying between 1 and $q$, then

$$r = (\nu - \tfrac{1}{2})\delta = \frac{2\nu - 1}{2q}.$$

We have then to find the sum

$$\Sigma.r\delta = \frac{1}{2q^2}\Sigma.(2\nu - 1)$$

for all values of $\nu$ from 1 to $q$; but we have

$$\Sigma.(2\nu - 1) = q(q + 1) - q = q^2;$$

so that

$$\Sigma.r\delta = \tfrac{1}{2},$$

and we have the simple expression

$$\tfrac{1}{4}NF\Omega$$

for the number of particles of a gas at rest as a whole which in unit time hit an area $F$ of the containing vessel. If for $F$ we understand, as at first, the area of an orifice in the side of the vessel, the expression we have found represents the number of particles which in unit time get to the orifice from the vessel.

The formula is deduced on the assumption that all the particles have the same speed $\Omega$. But it is easy to see that the formula also holds good if $\Omega$ denotes the mean of all the speeds that occur; it holds good, therefore, as is shown in § 41* of the Mathematical Appendices, even if the different values of the molecular speed are distributed according to Maxwell's law; it depends only on there being no difference in the distribution in different directions.

The number of particles getting into the orifice is not, indeed, the same as that which pass through it; for a portion will be pushed back by collisions with others. But the formula shows us that the speed of efflux of a gas must be simply proportional to the speed of its molecular motion.

The full meaning of this proposition comes out quite clearly only when we compare two different gases with each other. In both gases the speed of efflux must be determined in the same fashion by the mean molecular speed, since

Maxwell's and Avogadro's laws hold good for both. If both gases are under the same pressure $p$, the two equations

$$p = \tfrac{1}{8}\pi\rho_1\Omega_1^2, \quad p = \tfrac{1}{8}\pi\rho_2\Omega_2^2$$

hold good, $\rho_1$, $\rho_2$ being the densities of the two gases, and $\Omega_1$, $\Omega_2$ the mean speeds of their molecules. If, as in § 28, we refer the density not to that of water, but to that of air $D$, the formulæ take the form

$$p = \tfrac{1}{8}\pi D s_1\Omega_1^2, \quad p = \tfrac{1}{8}\pi D s_2\Omega_2^2,$$

and contain only the magnitude $D$ which varies with $p$, since the specific gravities $s_1$, $s_2$ are independent of pressure and temperature. These formulæ therefore give

$$s_1\Omega_1^2 = s_2\Omega_2^2,$$

and consequently

$$\Omega_1 : \Omega_2 = \sqrt{s_2} : \sqrt{s_1},$$

or the molecular speeds are inversely as the square roots of the specific gravities. In like manner the speeds with which different gases stream out into vacuous space are inversely as the square roots of the specific gravities of the gases. *The times required for efflux of equal volumes of different gases are therefore directly proportional to the square roots of the specific gravities of the gases*, these volumes being measured under the same pressure.

This law is confirmed by observation, in proof of which I subjoin some of Graham's[1] observed times of efflux of different gases, together with Regnault's and Henry's determinations of the specific gravities which he used.

| Gas | Square root of the specific gravity | Time of efflux through a | | |
|---|---|---|---|---|
| | | Drawn-out glass tube | Perforated brass plate | |
| Hydrogen | 0·263 | 0·277 | 0·276 | ... |
| Marsh gas | 0·745 | 0·756 | ... | 0·753 |
| Carbon monoxide | 0·984 | 0·987 | ... | ... |
| Ethylene | 0·985 | ... | ... | 0·987 |
| Nitrogen | 0·986 | 0·984 | 0·984 | 0·988 |
| Air | 1 | 1 | 1 | ... |
| Oxygen | 1·051 | 1·053 | 1·050 | 1·056 |
| Nitrous oxide | 1·237 | 1·199 | ... | ... |
| Carbonic acid | 1·237 | 1·218 | 1·197 | 1·209 |

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[1] *Phil. Trans.* 1846, p. 573.

The two series of experiments with the perforated brass plate were carried out with slightly different arrangements of the apparatus, and the second of these columns I have calculated from the results given by Graham for the speeds of efflux.

The agreement between the observed times and the square roots of the specific gravities may, on the whole, be considered excellent, and may serve as proof of the correctness of the theoretical law that has been established; it will not, therefore, be necessary to quote further observations made by Graham with altered values of the pressure. The greatest deviation from the law is exhibited by hydrogen, and, doubtless, for the reason assigned by Graham, that for this light gas, which undergoes very great friction in narrow tubes, the plate was not thin enough and the tube not short enough.

Not only does the law hold for the efflux of gases into vacuum, but the times of efflux of different gases are also proportional to the square roots of their specific gravities if under otherwise similar circumstances—especially, therefore, under equal pressures—they stream into a space filled with air or gas—the atmosphere, for instance.

The ground on which we are entitled to extend in this way the applicability of the law is very simple in the case of the back pressure being small in comparison with that which causes the efflux; the speed of efflux, in fact, will not be materially diminished by a slight resistance. The back pressure may, indeed, increase up to half the value of the pressure that forces out the gas without the speed sensibly falling off. This remarkable fact was first noticed by St. Venant and Wantzel,[1] and has been confirmed by later observers. On the kinetic theory we should explain the matter thus: that on issuing from the orifice and coming into the space which is less densely filled with gas, the molecules very seldom collide with others, since the latter also have most of them only just emerged from the orifice, and, therefore, for the most part are moving in the same direction and with nearly the same speed; they will therefore only seldom be overtaken by those that follow, and will stop them but little. The stream of molecules therefore flows into a less dense gas almost as it would into vacuum.

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[1] *Journ. de l'École Polyt.* xvi. 1839, p. 101.

But even if the pressure outside the containing vessel is not much less than that within, Graham's law still holds good. In this case the distribution of pressure in the orifice and its immediate neighbourhood is certainly quite different from that which accompanies efflux into vacuum. But if experiments are made with two different gases with the same two values of the pressures within and without, the pressures in the orifice itself will also be the same in both cases. The equation

$$p = \tfrac{1}{8}\pi D s_1 {\Omega_1}^2 = \tfrac{1}{8}\pi D s_2 {\Omega_2}^2$$

remains correct therefore in this case too. In like manner also, for the same reasons as in the former case, the speed of efflux is proportional to the molecular speed. Therefore Graham's law, which was deduced before from these two assumptions—the law, namely, that the times of efflux of two gases are as the square roots of the specific gravities—must hold good also for efflux into space already containing the gas. And if the space contains a different gas the law holds good in the same way.

This law of effusion is to such a degree confirmed by experiment that Leslie,[1] and later Bunsen,[2] have been able to found on it a method of determining specific gravities. Column I. of the subjoined table gives the values of the specific gravities determined by Bunsen by this method, and column II. those that have been calculated by Gay-Lussac's law (§ 30) from the atomic weights.

| Gas | I. | II. | Difference |
|---|---|---|---|
| Hydrogen | 0·079 | 0·069 | + 0·010 |
| Knallgas[3] | 0·414 | 0·415 | − 0·001 |
| Air | 1 | 1 | ... |
| Oxygen | 1·118 | 1·106 | + 0·012 |
| Carbonic acid | 1·535 | 1·520 | + 0·015 |

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[1] *Experimental Inquiry into the Nature and Propagation of Heat*, 1804, p. 534; *Gilb. Ann.* xxx. 1808, p. 260.

[2] *Gasometrische Methoden*, Braunschweig 1857, p. 127; 2nd ed. 1877, p. 184.

[3] [This is the mixture of hydrogen and oxygen produced by electrically decomposing water.—Tr.]

The deviation in the case of hydrogen has presumably the same cause as that shown in Graham's experiments.

## 38. Thermal Effusion

If the speed with which a gas issues from a narrow tube is really proportional to the speed of its molecular motion the two must increase in the same ratio when the temperature rises. From this it follows that it must be possible to augment the efflux of a gas by warming it. If we let a gas pass through a porous plate, we shall be able to increase its speed by warming the exit side of the plate.

A one-sided heating of the porous partition produced in this way is not only able to augment an already existing flow, but it is sufficient of itself, without any difference of pressure, to cause a percolation through the pores of the partition. Just as effusion results from a difference of pressure at the two sides of a porous partition, so can a similar phenomenon be brought about by a difference of temperature of the two sides of a partition ; and the latter phenomenon, according to Maxwell's[1] suggestion, is called *thermal effusion.*

The possibility of in this way producing a flow of gas by means of an unequal distribution of temperature was first pointed out by Carl Neumann[2] when he was attempting to explain the production of a thermoelectric current by analogy with a thermal effusion. At Neumann's suggestion Feddersen[3] arranged a simple experiment, in which he stuffed into a glass tube a tolerably long plug of spongy platinum and then warmed one of the ends of this plug ; he observed the phenomenon expected, viz. a flow of air through the plug from its colder to its warmer side. He obtained the same result on substituting hydrogen for air and spongy palladium for spongy platinum. He observed the same action, too, when he used other partitions made of gypsum, charcoal, silica, and burnt magnesium. Neumann and Feddersen called the phenomenon *thermo-diffusion.*

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[1] *Phil. Trans.* clxx. 1879, p. 255 ; *Scientific Papers*, ii. p. 711.

[2] *Ber. d. math.-phys. Cl. d. K. Ges. d. Wiss. zu Leipsig*, 1872, p. 49.

[3] *Pogg. Ann.* cxlviii. 1873, p. 302.

Osborne Reynolds,[1] who used the name *thermal transpiration,* repeated Feddersen's experiments, and made a great number of actual measurements of the difference of pressure that was produced at the warmer side of the partition. In the above-mentioned memoir Maxwell has given a very simple explanation of the phenomenon on the basis of the kinetic theory of gases. His theory starts from the assumption that the number of particles of gas which collide with the walls of the containing vessel in unit time is proportional not only to the number $N$ of molecules contained in unit volume but also to their mean speed $\Omega$; and, when the area struck is taken equal to unity, this number is expressed by the product

$$\tfrac{1}{4}N\Omega,$$

as in a formula developed in § 37.

If in unit volume on one side of the partition there are $N_1$ molecules with the mean speed $\Omega_1$, and on the other $N_2$ molecules with the mean speed $\Omega_2$, a unit area of the narrow openings in the wall will be met on one side by

$$\tfrac{1}{4}N_1\Omega_1$$

molecules, and on the other side by

$$\tfrac{1}{4}N_2\Omega_2.$$

If then

$$N_1\Omega_1 > N_2\Omega_2,$$

more molecules will pass over in the first direction than in the second, but fewer if

$$N_1\Omega_1 < N_2\Omega_2.$$

There consequently ensues a flow of gas from that side on which the product $N\Omega$ has the greater value towards that where the value is the smaller.

Suppose now, first of all, as is the case at the beginning of an experiment, that there is the same pressure on both sides of the partition; then between the values of $N$ and $\Omega$ there subsists the relation

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[1] *Phil. Trans.* clxx. pt. 2, 1879, p. 727; *Wied. Beibl.* vi. 1882, p. 455.

$$\tfrac{1}{8}\pi N_1 m \Omega_1^2 = \tfrac{1}{8}\pi N_2 m \Omega_2^2.$$

We have then

$$\Omega_1\sqrt{N_1} = \Omega_2\sqrt{N_2},$$

and consequently

$$N_1\Omega_1 > N_2\Omega_2$$

if

$$\sqrt{N_1} > \sqrt{N_2} \quad \text{or} \quad N_1 > N_2.$$

The flow of gas therefore proceeds in this case too from the side where there are the more molecules, *i.e.* where the gas is the denser, to the side where it is the less dense, just as in ordinary effusion; but while in this latter case the rarefaction is produced by lowering of pressure, in the case of thermal effusion just considered it is effected by warming. Hence the flow of a gas from a colder region to a warmer is a result of the theory no less than of experiment.

The pressure therefore rises on the warmer side, and a force opposing the motion is brought into play by which a state of equilibrium is finally set up; and we have now to investigate under what circumstances this will happen. The flow must cease when

$$N_1\Omega_1 = N_2\Omega_2.$$

In this case, between the values of the pressure on the two sides of the partition,

$$p_1 = \tfrac{1}{8}\pi N_1 m \Omega_1^2 \quad \text{and} \quad p_2 = \tfrac{1}{8}\pi N_2 m \Omega_2^2,$$

the relation

$$\frac{p_1}{\Omega_1} = \frac{p_2}{\Omega_2}$$

must hold. Introducing into this equation the absolute temperature $\Theta$ defined in § 15, and therefore putting

$$\Omega^2 = \Omega_0^2\Theta$$

in general, and in this particular case

$$\Omega_1^2 = \Omega_0^2\Theta_1, \quad \Omega_2^2 = \Omega_0^2\Theta_2,$$

we find as the condition of the final state of equilibrium

$$p_1 : p_2 = \sqrt{\Theta_1} : \sqrt{\Theta_2}.$$

The thermal effusion therefore ceases as soon as the ratio of the pressures on the two sides of the partition has attained the value of the ratio of the square roots of the absolute temperatures.

## 39. Heat Effects Accompanying Effusion

As effusion may arise from inequalities of temperature, so may it cause the temperatures at the two sides of a porous partition to be unequal. Cooling is produced at the side from which the flow takes place, while the other space into which the gas streams is warmed. The same action therefore occurs which has already been described in §§ 18, 19. Where the gas expands it cools, and where it is condensed it gets warmed.

The explanation of this behaviour[1] is also essentially that which has been given for the case in which it was assumed that the condensation was caused by the pushing down of a piston, the lifting of which made the gas to expand. The only difference consists in our having to take into account the encounters of the streaming particles with each other and with other particles instead of the collisions of the molecules against the piston.

A particle which reaches the orifice from the interior of the receiver does not here meet particles at rest, but particles in motion that are proceeding in the same direction. In consequence of this the particle will be thrown back into the receiver, not with the same speed with which it arrived at the orifice, but with a much less speed, while the motion of the particle that streams out is increased. Thus the particles in the receiver lose part of their molecular energy during the flow, and the gas in the receiver therefore cools.

On the other side of the partition the particles that escape from the orifice strike against particles that either are at rest or have lost in the larger space at least a part of their energy of flow by its transformation into heat. To these latter particles momentum is communicated by those which rush from the orifice with the full speed of the stream; the molecular motion therefore of the particles in the space into which the flow occurs is increased, or, what is the same thing, the temperature in this region rises by reason of the flow.

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[1] L. Natanson, *Wied. Ann.* xxxvii. 1889, p. 341.

Both conclusions agree with the experimental observations made by Joule and others.

# CHAPTER IV

## *IDEAL AND ACTUAL GASES*

### 40. Inexactness of the Theoretical Laws

ALTHOUGH all the laws which we have deduced from the kinetic theory of gases are in accordance with experiment, yet it must not, on the other hand, be overlooked that the agreement between observation and the strict results of theory has not proved to be absolutely complete and unexceptionable for any of the laws. In the case of Boyle's law respecting the pressure we have already had to remark that it holds good only approximately, and that every one of the gases shows deviations from this law, which, even if in most cases only small, are yet distinctly provable. This remark holds good also for all the other laws which follow from the theory. That Dalton's law with respect to the pressure of mixed gases suffers from the same deficiency as Boyle's cannot be doubted; from numerous observations which Galitzine[1] has partly made by himself and partly drawn from other sources, the pressure of a mixture is sometimes greater and sometimes less than the sum of the pressures exerted by the components separately. There must therefore be present several causes of different kinds which act together and cause the deviations from the theoretical laws in either the one direction or the other.

Just as incompletely do the experiments on the effusion of gases agree with the conclusions of theory. Neither does the speed of flow, as determined in Graham's and Bunsen's experiments, exactly correspond to the theoretical law, nor do the changes of temperature occur exactly as represented in § 39. Joule and Lord Kelvin have measured with great care the alterations of temperature that occur in the vessels from and to which the flow takes place, and by these observations have proved that the whole amount of work done by the gas in the receiver, when it flows out, is not to be found in the increased energy of the gas in the outer vessel which has been warmed by compression, and in the heat that has been produced by the overcoming of frictional resistances. This phenomenon has no explanation on our theory so far as it has been developed in the preceding chapters; it proves, therefore, that a secondary circumstance has not been sufficiently taken into account, and scarcely leaves room for doubt that the cause which has been neglected is the cohesion of the gases, to overcome which during their expansion into vacuum a part of the heat energy must be taken up.

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[1] *Das Dalton'sche Gesetz*, Strassburg 1890; *Wied. Ann.* xli. 1890, p. 588; *Gött. Nachr.* 1890, p. 22.

If we take in hand a thorough comparison of the two laws which bear Gay-Lussac's name with the results of experiment, we see no less clearly that our theory has not so far led us to absolutely strict laws of nature, but only to rules that hold good approximately, though the approximation is certainly excellent.

According to the first of these, all gases are to expand equally under the action of heat; they ought, therefore, all to have the same coefficient of expansion as air, viz. 0·00367. But the value of this coefficient is, for instance, 0·00366 for hydrogen and 0·00370 for carbonic acid. Similar deviations, which in some cases are even larger, are exhibited by other gases too.

Indeed it cannot be said of any one and the same gas that under all circumstances it has the same coefficient of expansion. Magnus[1] has pointed out that the coefficient of expansion must vary if Boyle's law is not exactly obeyed. For if the pressure and volume of a gas are not strictly inversely proportional to each other, there is no reason to expect that both magnitudes will be increased in exactly the same ratio by a rise of temperature. We have therefore, strictly speaking, two different thermal coefficients to distinguish in a gas, viz. the coefficient of *volume*-increase and the coefficient of *pressure*-increment; the former determines the increase of volume that occurs with rise of temperature when the pressure remains constant, and the latter measures the increase of pressure that is produced by heating without change of volume. By his experiments Regnault proved the difference of these coefficients; he found, indeed, that with most gases the volume-coefficient is somewhat larger than the pressure-coefficient, hydrogen alone showing the reverse property. Regnault[1] further observed that the two coefficients are not entirely independent of the pressure and temperature of the gas, but that they increase with the pressure and diminish when the temperature rises.

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[1] *Pogg. Ann.* lv. 1842, p. 5.

This behaviour of gases may be also indirectly recognised from the observations that have been made on the specific gravities of gases. These are usually referred to the density of atmospheric air, at the same pressure and temperature, as unity. It is therefore sufficient to determine the specific gravity of a gas at different temperatures in order to learn whether this gas has the same mean coefficient of expansion as air, or a different one that varies with the temperature or the pressure.

An instructive example is given by the experiments made by E. Ludwig[2] on the density of chlorine. For the densities of the gas, compared with air, he found the following values:—

| | | | |
|---|---|---|---|
| 2·481 | at | 20° | C. |
| 2·478 | ,, | 50° | ,, |
| 2·468 | ,, | 100° | ,, |
| 2·461 | ,, | 150° | ,, |
| 2·450 | ,, | 200° | ,, |

The falling-off in these numbers shows that chlorine expands more than air. At 200° chlorine attains the same density as it should have according to Gay-Lussac's law in § 30; presumably from this temperature upwards its specific gravity remains constant, so that its expansion-coefficient would have become equal to that of air, while at lower temperatures it must be greater.

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[1] *Mém. de l'Acad. de Paris*, xxi. p. 96; xxvi. p. 565.

[2] *Ber. d. deutsch. chem. Ges.* i. 1868, p. 232.

## 41. Vapours

With vapours developed from liquids by heat the deviations from the theoretical laws are much larger than with gases proper. On the whole, vapours comport themselves as gases. They obey Boyle's law approximately, so that in their case, too, the pressure and volume vary very nearly in inverse proportion; and further, both pressure and volume increase with rising temperature in almost equal ratio, just as with gases. Dalton's law also holds good for mixtures of vapours and gases with approximate exactness. We might, therefore, apply the kinetic theory also to vapours by ascribing to their molecules, just as to those of gases, a rapid rectilinear motion, and by assuming that this motion increases with the heat.

Whether and how far these assumptions suit a given case can be most easily determined from the vapour-densities. As *vapour-density* we denote the value obtained for the specific gravity of a vapour when the density of air at the same pressure and temperature is taken as unity. The vapour-density must, therefore, be independent of pressure and temperature if the vapour obeys Boyle's and Gay-Lussac's laws as exactly as air. Observation has shown that only within certain ranges of pressure and temperature can a vapour-density be looked on as constant.

In such determinations experiment has in general shown that greater values of the vapour-density are found the lower the temperature at which the measurement is made, and that not till higher temperatures are reached do we observe a constant density of the vapour, *i.e.* a density independent of the temperature. Further, for greater values of the pressure we likewise find greater values of the density of a vapour, as compared with air under equal pressure; and, correspondingly, the vapour-density approaches constancy in its value as the pressure falls off.

As regards the coefficient of expansion, it follows from the reasons given that it is not at all constant under all circumstances, but that it depends on temperature and pressure in such wise that with rising temperature or falling pressure it decreases, and that at a sufficiently high temperature or a sufficiently low pressure the expansion-coefficient for every vapour attains the same value as that of atmospheric air.

## 42. Saturated Vapours. Absolute Boiling-point

A problem to which the endeavours of experimentalists in this direction have been especially directed consists in the measurement of the highest pressure which a vapour can attain in dependence on the temperature. The theoretical investigators have also occupied themselves very greatly with the condition of vapours at their maximum pressure, or of *saturated* vapours, as they are called. Interesting as are these researches, and important as their results may be in themselves, this limiting case has less significance for the theory of *gases* than for a corresponding theory of *liquids*.

For the state of equilibrium of a saturated vapour which lies above its liquid is characterised by this, that the equilibrium is maintained by vaporisation and condensation at the surface of the liquid. The molecules of the vapour which in their to-and-fro motion strike the liquid surface will not all bounce back, but a part will be retained by the force of cohesion. On the contrary, it will happen just as often that a particle of fluid which possesses sufficient speed tears itself loose from its neighbours, and passes into the vapour above. From this it follows that, in the state of equilibrium of a saturated vapour, the kinetic energy of the vapour is equal to the work which is done by the forces of cohesion during condensation to the liquid state. The measurement of the *maximum* pressure of the vapour has therefore this significance, that it gives a measure for the energy-value of cohesion in the *liquid* state, while for the determination of the properties and laws of the vapour state the observation of unsaturated or superheated vapours is of greater importance.

We shall, therefore, here touch upon only one point of especial interest which has resulted from the observations of Mendelejeff[1] and Andrews.[2] As the observations of Frankenheim and others on the capillary rise of liquids in narrow tubes at different temperatures have shown, the cohesion of a liquid decreases greatly as the temperature rises, whence we should conclude that heat probably produces molecular motions in liquids, just as in gases, by which their cohesion is diminished. If we increase the temperature and this molecular motion more and more by addition of heat, we may imagine a point reached at which the forces of cohesion cease to act and the capillary constant which measures them is zero.

On the other hand, the vaporisation which results from the rise of temperature and the consequent increase of molecular motion is prevented, or at least hindered by pressure. We may imagine the process to be this: that pressure and diminution of volume bring the molecules of the vapour nearer together, and cause their cohesive forces, which increase with diminishing distance between the molecules, to come more strongly into play, so as to overcome the expansive force due to the motion of the molecules. This is, however, possible only so long as the kinetic energy of the molecular motion is not too great; if by the addition of heat this energy should become so great as to exceed the sum total of the potential energy of the forces of cohesion which is lost by two molecules which, from being widely separated, come into contact with each other, it is no longer possible to cause the molecules to join together, and it is, therefore, also no longer possible for the vapour to be changed into liquid by pressure. The temperature necessary for this, which Mendelejeff calls the *absolute boiling-point*, may, according to our former remarks, be determined also from the diminution of the capillarity with rise of temperature. Mendelejeff has determined the height of this point for several liquids.

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[1] *Ann. Chem. Pharm.* cxix. 1861, p. 1; *Pogg. Ann.* cxli. 1870, p. 618.

[2] *Report Brit. Ass.* 1861, ii. p. 76; *Ann. Chem. Pharm.* cxxiii. 1861, p. 270; *Phil. Trans.* clix. pt. 2, 1869, p. 575; *Pogg. Ann.* Erg.-Bd. v. 1871, p. 64; *Proc. Roy. Soc.* xxiii. 1875, p. 514.

These theoretical views are in most excellent agreement with the observations made by Andrews, and also earlier by Cagniard de la Tour and Faraday. Andrews called the temperature of the absolute boiling-point, the *critical point*, which forms the limit between the vapour state and that of a gas proper. At a temperature below this critical point an elastic fluid can be condensed into a liquid both by pressure and by cooling, that is, by either alone, and thus deserves the name *vapour*. On the contrary, at a temperature above the critical point there is no pressure high enough of itself to make the fluid become liquid, and both cooling and pressure must be applied together to produce condensation; the fluid is then called a *gas*.

Conformably to Mendelejeff's theoretical interpretation, therefore, we must consider a *gas* to be a medium in which the kinetic energy of the molecules is greater than the sum total of the energy of the forces of cohesion which may come into play on condensation to a liquid. In a *vapour*, on the contrary, the energy of motion does not reach this amount, but it is sufficient to overcome the part of the cohesion-energy which from time to time comes into play in the to-and-fro motions of the vapour molecules.

A further investigation of these interesting limiting states between gas, vapour, and liquid that have been touched upon, and especially of the saturated state of vapours, will some day or other[1] presumably form a bridge by which a passage will be found from the kinetic theory of gases to a kinetic theory of liquids—a theory the ideas underlying which have been already expressed by Clausius.

For us, whose aim is the establishment of the laws of gases, the foregoing suffices, on the one hand, to show the necessity of an improvement of our theory, which has otherwise approved itself in so many different respects, and, on the other, to point out the means by which the defects that have clung to it so far may be removed. The chief ground of these defects we shall have to seek in our having hitherto taken no account of the cohesion of gases.

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[1] [Voigt has elaborated a kinetic theory of vaporisation and of liquids in *Gött. Nachr.* 1896, p. 341; 1897, pp. 19, 261. See *Phys. Soc. Abstracts*, iii. 1897, p. 350; *Science Abstracts*, i. 1898, p. 545.—Tr.]

## 43. Rankine's and Recknagel's Modification of Boyle's Law

An attempt to carry the kinetic theory further in this direction, and to find the correction of Boyle's law that is necessitated by cohesion, has been already made by Rankine[1] and by Recknagel[2] with happy results. Recknagel allowed for the influence of the cohesion of the gas, in the calculation of the pressure exerted by it, by assuming at every encounter between two molecules a temporary retardation of their rectilinear motions—what, in fact, might be the simplest way of taking the influence of the curvature of the paths into account. Joule's calculation of the pressure given in § 11 will hereby be so far altered that the number of collisions of a particle in unit time against the wall will be diminished by an amount which increases with the number of collisions made by the particle with other particles. We may, therefore, assume this diminution to be directly proportional to the density of the gas, or inversely proportional to its volume, and thereby obtain for the pressure, the value of which is proportional to this number, not Boyle's law as before, but a more general formula of the shape

$$pv = A(1 - Bv^{-1}),$$

where $A$ and $B$ are magnitudes depending on the temperature only; and according to Rankine $A$ is directly and $B$ inversely proportional to the absolute temperature.

This formula agrees well with the experimental results obtained in 1862 by Lord Kelvin and Joule[3] on the cooling that accompanies the expansion of gases. Recknagel also finds that the formula represents Regnault's observations on the compressibility of carbonic acid with great exactness; since it gives a maximum value for $p$, this occurring for $v = 2B$, it suffices also to represent Regnault's determinations of the maximum pressure of the gas as a function of the temperature. It thereby appears —what deserves to be mentioned as especially important— that the saturated vapour of carbonic acid has the same thermal coefficient of expansion as the permanent gases.

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[1] Note in a Memoir by Thomson and Joule, *Phil. Trans.* cxliv. 1854, p. 336.

[2] *Pogg. Ann.* Erg.-Bd. v. 1871, p. 563.

[3] *Phil. Trans.* clii. 1862, p. 588.

This is, however, not an incontestable proof of the exactness of the hypothesis from which the formula was deduced. For exactly the same formula comes also from the different assumption that in condensable gases a part of the molecules are bound together in pairs, since with this hypothesis we have to take into account a diminution of the number of colliding molecules, which diminution is to be assumed the greater the oftener the molecules collide together, that is, the more particles there are in unit volume.

## 44. Hirn's and van der Waals's Correction of Boyle's Law

For the same reason a more general theory, which we owe to Hirn[1] and to van der Waals,[2] leads also to the same result, without its appearing necessary to specialise the hypothesis so exactly.

This theory not only considers the force of cohesion, which alone up to the present has been mentioned as a cause of the deviations from Boyle's law, but also takes into account, as a second cause, the circumstance that has been mentioned before (§ 8), viz. that the dimensions of the molecules are of disturbing influence on the exactness of the law. This necessitates a twofold change in the theoretical formula

$$p = \tfrac{1}{3}NmG^2,$$

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[1] *Théorie Mécanique de la Chaleur*, ii. 1864, p. 215; *Ann. Chim. Phys.* [4] xi. 1867, p. 47.

[2] 'Over de continuïteit van den gas- en vloeistof-toestand,' *Academisch Proefschrift*, Leiden 1873. Translated into German by F. Roth, Leipsig 1881 [and thence into English for the Physical Society of London]. Abstracted in *Pogg. Beibl.* i. 1877, p. 10.

which may also be written

$$\tfrac{1}{2}nmG^2 = \tfrac{3}{2}pv,$$

if we introduce the number $n$ of molecules in the volume $v$ instead of the number $N$ contained in unit volume.

In its new shape the formula shows itself as an application of the theorem of the conservation of energy to the system of $n$ molecules, by stating that the energy of motion represented by the term on the left-hand side of the equation finds its equivalent in the volume $v$ being filled at the pressure $p$. If the medium has internal cohesion, this pressure is not the only equivalent, but there is another pressure arising from the cohesion that must be added to $p$ in the preceding equation.

On the other hand, the volume $v$ of the gas which occurs in the equation must be diminished if the molecules occupy space; for the molecules fly about here and there, not in the whole of the space filled with the gas, but in that part which is left free between them. The number of collisions, therefore, depends only on the extension of this space that is left free, and not on the whole of the volume filled. The intensity, therefore, of the pressure exerted will also be determined only by this smaller volume.

The theoretical formula consequently needs correction on both grounds, and we must put

$$\tfrac{1}{2}nmG^2 = \tfrac{3}{2}(p + \mathfrak{C})(v - b),$$

where $\mathfrak{C}$ denotes the pressure arising from the cohesion, and $b$ the space by which the volume $v$ has to be diminished.

Of the two new magnitudes introduced, the latter $b$ is made up of the sum of the volumes which are so filled by the $n$ molecules that no other molecule could force its way into any one of them. Possibly the volume filled by a molecule in this sense is actually determined by its own extension in space; a different assumption, however, is quite possible. Physicists who believe in a luminiferous ether, which is different from ponderable matter, would be disposed to consider the volume of the *ether atmospheres* condensed about the atoms rather than that of the molecules. The assumption of Clausius, Maxwell, and others is also permissible, namely, that the forces acting between the molecules drive two encountering molecules away from each other even before the moment of an actual contact. We should then have to consider not the actual space occupied by the molecules, but the sum of larger spaces which surround the molecules; and since we might picture these envelopes as spherical, we might justify the name *molecular sphere*, which we will retain until in our investigation of the free path (§ 63) we introduce the term *sphere of action*, used by Clausius, for a sphere with a similar meaning.

One is tempted to take the magnitude $b$ that occurs in the formula simply as the sum of the molecular spheres; but this conclusion could be unhesitatingly pronounced right only if the molecules could be supposed at rest. But as they move about they mutually obstruct each other by their motion in greater proportion than if they were partly at rest; it consequently follows that we shall have to understand by $b$ a multiple of the sum of the molecular spheres. The more exact determination of this we shall leave for Part III. (§ 117); at present the remark is sufficient that, excepting perhaps the most extreme cases, we have to represent by $b$ a magnitude which, as well as the molecular sphere, is independent of the pressure and volume.

The second magnitude $\mathfrak{C}$ contained in the corrected formula, viz. the pressure which results from the forces of cohesion, is determined by van der Waals in the same way as Laplace calculated, in his theory of capillarity, a magnitude of similar meaning, which he denoted by $K$, viz. the pressure against a flat bounding surface. Since each of these pressures, both $\mathfrak{C}$ and $K$, arises from the mutual actions of attracting and attracted particles, it is proportional to the number of attracting particles on the one hand, and of attracted particles on the other; and it is consequently proportional to the square of the number of particles present, and thus increases in proportion to the square of the density. If we refer all magnitudes varying with the expansion of the gas to the volume, as in the last formula, and not to the density, we have to introduce $\mathfrak{C}$ as a magnitude inversely proportional to the square of the volume containing the gas.[1]

Hence van der Waals's corrected formula for Boyle's law becomes

$$\tfrac{1}{2}nmG^2 = \tfrac{3}{2}(p + av^{-2})(v - b),$$

wherein $a$ and $b$ are constants independent of the pressure and volume; and if, as before, we express the molecular speed by the temperature,

$$(p + av^{-2})(v - b) = R(1 + \alpha\vartheta),$$

where $R$ is a constant, and $\alpha$, $\vartheta$ denote, as before, the coefficient of expansion of gases and the temperature. Only by comparison with experiment can it be determined whether $a$ and $b$ depend on the temperature; van der Waals finds that it is tolerably sufficient to assume them both to be independent of the temperature, as well as $R$ and $\alpha$.

## 45. Comparison with Regnault's Observations

The theoretical formula obtained agrees nearly exactly in form with the formula of interpolation by which Regnault represented the results of his observations; for this has the form [2]

$$\frac{r}{m} = 1 - A(m - 1) + B(m - 1)^2,$$

wherein $m$ denotes the ratio of two values of the volume reduced to the same temperature, say 0° C., or

$$m = V/v,$$

$r$ that of the corresponding values of the pressure,[3] or

$$r = p/P,$$

while $A$ and $B$ are constant coefficients. If, as in Regnault's memoir, that volume $V$ is taken as unity which, at the pressure $P = 1$ metre of mercury, is filled by the mass of gas used in the experiment, Regnault's formula can be more simply written

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[1] Ritter has proceeded by this method in determining the cohesion of gases in a memoir (*Mém. de la Soc. de Phys. de Genève*, xi. 1846, p. 99), with which I have become acquainted only through the notice of it by von Morozowicz in the *Fortschritte der Physik*, ii. 1846, p. 89.

[2] *Mém. de l'Acad. de Paris*, xxi. p. 421.

[3] See Table of Errors at the end of vol. xxvi. of the *Mémoires*.

$$pv = 1 - A\left(\frac{1 - v}{v}\right) + B\left(\frac{1 - v}{v}\right)^2,$$

or

$$pv + (A + 2B)v^{-1} - Bv^{-2} = 1 + A + B.$$

In this form it agrees with the theoretically deduced formula of van der Waals for the temperature 0°, viz.

$$pv + av^{-1} - bp - abv^{-2} = R,$$

if it is allowable to replace the pressure in the correction term $bp$ by the reciprocal of the volume in accordance with the approximately correct Boyle's law

$$p = \frac{PV}{v} = v^{-1};$$

for then van der Waals's formula runs

$$pv + (a - b)v^{-1} - abv^{-2} = R,$$

so that it is equivalent to Regnault's if the constants calculated for unit of mass are related to each other according to these equations:—

$$\begin{aligned} a - b &= A + 2B, \\ ab &= B, \\ R &= 1 + A + B. \end{aligned}$$

Under these circumstances a detailed comparison of the formula with the numbers obtained directly is not necessary. But it should be mentioned that from the values of $A$ and $B$ found by Regnault we shall afterwards be able to calculate[1] the numerical values of $a$ and $b$, which represent the magnitude of the cohesion and the extension in space of the molecules.[2]

## 46. Pressure- and Volume-coefficients

Van der Waals's formula is also suitable for explaining the variation in the values of the expansion-coefficients, and especially the circumstance that the coefficient which determines the increase of pressure with temperature is not identical with that on which the increment of volume depends.

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[1] Van der Waals, *Continuïteit*; Roth, *Wied. Ann.* xi. 1880, p. 1.

[2] See Chap. X.

The value of the former coefficient, which for distinction from the other—the expansion-coefficient proper—may be termed the *pressure-coefficient*, is the more easily obtained. The increase which the pressure of a gas undergoes when the temperature is raised from 0° to $\vartheta$ while the volume remains unchanged is found by comparison of the formula

$$(p + av^{-2})(v - b) = R(1 + \alpha\vartheta)$$

for the latter temperature with that referring to 0°,

$$(p_0 + av^{-2})(v - b) = R,$$

when we give to $v$ the same value in both. By subtraction we get

$$(p - p_0)(v - b) = R\alpha\vartheta$$

or

$$p - p_0 = (p_0 + av^{-2})\alpha\vartheta,$$

whence we obtain for the pressure-coefficient the corrected formula

$$\alpha_p = \left(1 + \frac{a}{p_0 v^2}\right)\alpha.$$

This teaches that gases in which cohesion really exists have a greater pressure-coefficient $\alpha_p$ than the ideal gases for which its value is $\alpha$. Since this behaviour agrees with experience, the formula can be used to deduce the value of the constant $a$, which measures the strength of the cohesion, from the observations.

The same agreement between theory and observation is also shown when we calculate from the theoretical formulæ the value of the expansion-coefficient proper, *i.e.* that coefficient which determines the increment of volume. Since $p$ is now to be taken as constant and $v$ as variable, the formulæ

$$(p + av^{-2})(v - b) = R(1 + \alpha\vartheta),$$
$$(p + av_0^{-2})(v_0 - b) = R$$

give for the expansion-coefficient defined by the formula

$$\alpha_v = \frac{v - v_0}{v_0 \vartheta}$$

the value

$$\alpha_v = \frac{(p + av_0^{-2})(1 - bv_0^{-1})}{p - av^{-1}v_0^{-1}\{1 - b(v^{-1} + v_0^{-1})\}}\alpha.$$

In order to gain an insight into this complicated formula let us apply it to extreme cases, and first of all to that, approximately realised with hydrogen, in which $a = 0$ or the cohesion is vanishingly small. With this assumption we have

$$\alpha_v = (1 - bv_0^{-1})\alpha,$$

so that

$$\alpha_v < \alpha \quad = \alpha.$$

Now, on the contrary, take the cohesion to be so great that in comparison with it we may neglect the correction that arises from the size of the molecules, or put $b = 0$; then

$$\alpha_v = \frac{p + av_0^{-2}}{p - av^{-1}v_0^{-1}}\alpha;$$

in this case therefore we have

$$\alpha_v > \alpha_p > \alpha.$$

Both of these conclusions from theory are in consonance with experiment; for according to Regnault's observations already mentioned in § 40 we have for hydrogen

$$\alpha_v = 0{\cdot}003661, \quad \alpha_p = 0{\cdot}003667;$$

but for all other gases the relation between the values of the coefficients required for the second case is fulfilled.

Van der Waals's theory thus agrees in all points with experiment in so far as it rightly expresses the general laws. This agreement speaks for the fact that to a certain degree the assumptions on which the theory rests correspond to reality. If we should consider van der Waals's theory also as probably not yet perfect, we are yet justified in the view that in it the first step is taken along the path by which we shall arrive at a completely satisfactory kinetic theory of real gases and not of ideal gases only. The point in which it most especially needs improvement is the manner in which the law of cohesion is introduced.

### 47. Completions of van der Waals's Formula

Properly recognising this imperfection, Clausius[1] has attempted to improve van der Waals's formula by substituting another expression for the value of the cohesion. His formula, which has the form

$$\{p + a(v + \beta)^{-2}\}(v - b) = R(1 + \alpha\vartheta),$$

differs from that of van der Waals essentially in this: that the cohesion-pressure is put inversely proportional, not simply to the square of the volume $v$, but to the square of the volume $v$ increased by a constant $\beta$. By this means Clausius obtains a better agreement of the formula with observations that have been made under high pressures, and therefore with small volumes.

Ramsay and Young[2] think it more correct to substitute the more general expression of an $n$th power instead of that of the square of the volume $v$.

A second difference between the formulæ of Clausius and van der Waals consists in this: that the magnitude $a$ is with Clausius not a constant, but a function of the temperature. As he first employed his formula only in the case of carbonic acid, he could be content with the assumption of the simple formula

$$a = \frac{c}{\Theta},$$

in which $c$ is a constant and $\Theta$ denotes the absolute temperature

$$\Theta = \vartheta + \alpha^{-1}.$$

Later on, when trying to apply the formula to other gases and vapours, he assumed a more general expression,

$$a = (A\Theta^{-n} - B)R(1 + \alpha\vartheta),$$

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[1] *Wied. Ann.* ix. 1880, p. 337; xiv. 1881, pp. 279, 692; *Mechanische Wärmetheorie*, 1889-91, iii. pp. 184, 215, 227.

[2] *Proc. Roy. Soc.* xlii. 1887, p. 5.

in which $A$, $B$, $n$ are constants. Similarly Battelli[1] put

$$a = (A\Theta^{-n} - B\Theta^{m})R(1 + \alpha\vartheta),$$

so that he had one more constant at his command. G. Jäger,[2] on the contrary, added to $a$ the factor

$$\Theta^{-1}e^{\gamma/\Theta},$$

where $\gamma$ is constant.

These formulæ exhibit much better agreement with experiment than the simpler formula of van der Waals, as is to be expected from the greater number of disposable constants. Yet, as Korteweg[3] has remarked, the formula of Clausius deviates from the observed behaviour of gases in many other regards more largely than that of van der Waals. For our theory the more complicated formulæ are less valuable than the original simpler one on account of the difficulty of their interpretation.

Amagat[4] has completed van der Waals's equation by giving it the form

$$\{p + Av^{-3}(v - \varepsilon)\}\{v - b + B(v - b)^{n}\} = R(1 + \alpha\vartheta),$$

which contains five constants, $A$, $B$, $\varepsilon$, $b$, $n$. This formula has proved itself good in a comparison with the observed behaviour of hydrogen.

Boltzmann and Mache[5] assume the formula

$$(p + av^{-1})(v - b) = R(v + 2b)(1 + \alpha\vartheta).$$

## 48. The Cohesion of Gases

If it can appear scarcely doubtful that the defects of the theory, even after the corrections just applied, depend on the cohesion having been insufficiently treated, there may yet arise doubts as to the mode in which a strict theory

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[1] *Memorie di Torino* [2] xliv. 1893, p. 27.

[2] *Wiener Ber.* ci. 1892, p. 1675.

[3] *Wied. Ann.* xii. 1881, p. 143.

[4] *Comptes rendus*, cxviii. 1894, p. 566. [He has also found (*Comptes rendus*, cxxviii. 1899, p. 538) that the behaviour of $CO_2$ in a very wide range of pressure and temperature is well represented by a formula of the type

$$p + \frac{v - \{a + m(v - b) + c(v - b)^{-1}\}(1 + \alpha\vartheta)}{kv^{n} - \alpha + \sqrt{\{(v - \beta)^{2} + d^{2}\}}} = R(1 + \alpha\vartheta)v^{-1}.\text{—Tr.]}$$

[5] *Wiener Sitzungsanzeiger*, 1899, p. 87.

would have to take the influence of this force into account, and as to the change in our views regarding molecules and their motion that are demanded by reason of the cohesion. There are, in fact, two essentially different explanations of the deviations which gases and vapours exhibit from the theoretical laws, and yet both explanations arise at bottom from the same origin.

In order to understand this double possibility we need only remember that the foundation of our theory contains also several unproved and unprovable assumptions, of which only two come here into account. The first is the assumption that gases consist of molecules *of invariable mass*, the second is the hypothesis that they move in *straight* lines.

Of these two hypotheses the latter at first sight seems the more doubtful; for in any case it is only true with the limitation or exception that at the moment of a collision the motion, till then along a straight line, must experience a sudden change of direction. But the former, too, as we shall see, is not above doubt, and an inexactness in this hypothesis might just as well cause the deviations as an error in the second of the two hypotheses.

We can frame for ourselves no idea of the cohesion of gases that is essentially different from that of liquids; we imagine, therefore, forces which act attractively from particle to particle in the direction of the line joining them, and whose strength falls off very quickly as the distance increases, so that at a finite or measurable distance the force is infinitely small. It would be as difficult to oppose this customary supposition regarding the nature of cohesion as to contest the essential part of the kinetic theory of gases if we were to ascribe to the forces of cohesion, for a distance of the attracting particles from each other equal to the *mean* distance apart of those which were the nearest neighbours, a sensible value which comes somehow into consideration. We shall therefore have to assume that attractive forces of any importance are active between two particles only when they actually collide or just graze each other in their paths.

If we assume this idea of the action of the force of cohesion, we do not on this account need to drop the hypothesis of rectilinear motion, in which the most essential and characteristic peculiarity of Bernoulli's theory consists. It only becomes necessary to modify the hypothesis so that the changes of direction from one straight path to another are not caused suddenly by a collision, but gradually by forces which act continuously, even if they very quickly come into and go out of play. The paths then do not form sharp-angled zigzag lines, but the passage from one straight line to another is brought about by lines that are sharply but continuously curved so that the corners seem to be rounded off. In the next paragraph we shall have to discuss, at least in its general character, the influence which this modification of the hypothesis introduces into the calculation of the pressure.

Still, an effect of quite a different kind is conceivable with the same hypothesis as to the nature of cohesion.[1] If we assume, with regard to this force, that it acts only in the proportionately rare moments of an actual or very nearly occurring collision between two molecules, the fact established by Joule and Lord Kelvin, that the intensity of the cohesion in gases is very small, will be simply explained by the force acting only during the short time of the collision and being in abeyance during the much longer interval between successive collisions. There would therefore be no contradiction with the observations mentioned if we assume that in the short periods of collision the force acts with very considerable intensity.

But if this assumption is admissible there is nothing inconsistent in the hypothesis that the attractive forces of cohesion might be able, at least now and then under favourable circumstances, to bind together two colliding particles so fast that they traverse the next stretch of their path together as a double molecule. By this a state of equilibrium would be produced in the gas in which, among the molecules of the same kind, there would be always some of greater mass. The number of the latter would depend on the frequency of the favourable cases of collision, and therefore, also, chiefly on the number of collisions that occur, so that in a denser gas wherein the molecules collide more frequently there will be also more molecules of greater mass.

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[1] In his memoir on 'Temperature and the Measure of Temperature' (*Pogg. Ann.* Erg.-Bd. vi. 1874, p. 275) Recknagel also considers effects of two kinds—attraction of molecule on molecule and actions within molecules. The latter are perhaps to be interpreted in the manner explained later.

## 49. Playfair and Wanklyn's Explanation of the Anomalies

The hypothesis last expounded forms the basis of the explanation of the anomalies regarding vapour-densities that has been given by Playfair and Wanklyn,[1] an explanation which embraces all the other deviations of actual gases from the theoretical laws.

According to what has already been said regarding the hypothesis, it is only necessary to remember the mechanical definition of temperature, given before in § 14, to see at once the possibility of the explanation of all anomalies. According to § 29, the mean value of the kinetic energy of a molecule, even when of different kinds, forms the measure of temperature. Consequently, in a gas whose molecules are either wholly or in part bound together to form larger aggregates, the kinetic energy contained in unit volume is less than before the aggregation; or, more simply expressed, the pressure is lowered by the aggregation of molecules if the rise of temperature resulting therefrom is compensated. Hence a gas whose molecules may combine together may be more easily and strongly compressed than an ideal gas whose molecules are unalterable massive points. A deviation from Boyle's law will therefore arise in the direction shown by most of the gases included in the table of § 7, with the single exception of hydrogen, the behaviour of which has been already described elsewhere; and determinations of vapour-density will therefore give higher values the higher the pressure during the measurement, as was found, for instance, by Alex. Naumann to be the case for acetic acid.

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[1] *Trans. Roy. Soc. Edin.* xxii. pt. 3, 1861, p. 441; *Ann. Chem. Pharm.* cxxii. 1862, p. 247.

The fact that the vapour-density is smaller at higher temperatures and larger at lower temperatures is explained in the same way; for since the heat-motion loosens the bond between the molecules the molecules will be lighter, and therefore the gas or vapour will be specifically lighter at the higher than at the lower temperatures.

The behaviour of the thermal expansion-coefficients is also directly explained. At lower temperatures not only do the gaseous molecules separate more widely from each other on the addition of heat, but they also split up and require greater space for their greater number. At higher temperatures, at which all the molecules have been already split up, heating brings about merely an increase of speed as in ideal gases; all vapours and condensable gases must therefore at high temperatures attain the same thermal coefficients of expansion as the so-called permanent gases, while at lower temperatures they expand more largely.

If this explanation of the deviations is really true, a conclusion already drawn by Regnault[1] from his observations on the compressibility of gases must be unconditionally considered as correct. If molecules that are bound together are more and more separated by rise of the temperature, there must be a temperature at which all move singly and no further separation is possible; at this temperature the ground in question of the anomalies would fail, so that the only cause of an anomaly that would remain is the circumstance that the dimensions of the molecules in comparison with their distances apart need not be vanishingly small, a cause therefore which, as in hydrogen, would entail a deviation in the opposite direction. According to this theory, therefore, as Regnault has already conjectured, every gas must at a sufficiently high temperature exert a greater pressure than would be expected by Boyle's law, and a less pressure at lower temperatures, so that for every gas there will be a certain temperature at which it strictly obeys this law. Hydrogen would at very low temperatures behave just like the others.

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[1] *Mém. de l'Acad. de Paris*, xxi. 1847, p. 404.

## 50. Horstmann's Explanation

A different explanation of the same circumstances given by Horstmann[1] rests at bottom on the second of the hypotheses described in § 48, although Horstmann gives it a quite different form. He throws doubt, in fact, on the exactness of Avogadro's law in the case of vapours and gases which do not strictly obey Boyle's law, and explains it as being only approximately correct. This law is, on our theory, a necessary consequence of the hypothesis that pressure and temperature are caused by rectilinear motion of the molecules alone. Hence Horstmann's assumption is not essentially different from that discussed in § 48, according to which the to-and-fro straight paths of the molecules are supposed to be joined together by curved parts.

By this assumption also the observed anomalies can be explained. The force of the blow with which a molecule strikes against the wall of the space filled with gas or vapour is greater if the molecules move in right lines free from forces of cohesion than if they are drawn back from the wall and into the interior of the space in curved paths by the attraction of other molecules. The pressure, therefore, of a vapour or gas which contains a given number of molecules will be the less the more frequently the molecules are caused to move in curved paths, and the greater the more frequently and the longer they move in straight paths. If, therefore, the density is increased, the pressure increases, not in the same ratio, but in a less degree, because the increase of the number of collisions causes a diminution of the force of a collision. On the other hand, by an increase of temperature the pressure will increase in greater measure, since the force of a blow increases not only for the reasons already given, but also because the faster moving molecules traverse longer straight paths.

These views, therefore, also suffice to explain simply and naturally not only the greater vapour-density possessed by easily condensed gases and vapours in the neighbourhood of their condensing point, but also the fact that their volume- and pressure-coefficients are greater than those of ideal gases.

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[1] *Ann. Chem. Pharm.* Suppl. Bd. vi. 1868, p. 53 ; also in his *Habilitationsschrift*, Heidelberg 1867.

## 51. Claims of the Two Explanations

In the present position of the matter a definite answer to the question, Which of the two explanations of the anomalies deserves preference? is not possible, since each represents the observed behaviour in general, and neither seems to contradict our gaseous theory, which is otherwise confirmed. A distinction between them could only be made after a further pursuit into details of the views that have only been sketched very generally.

In order to carry out the theory of gases with the suggested corrections in the one direction or the other, the calculus of probabilities offers the same method as was used to prove Maxwell's law of speeds. It would be only necessary to consider as unknown not only this law of distribution, but also the form of combination of the molecules, whether in groups or as units. The problem offers the same difficulties as a mathematically formulated chemical statics, which would have to treat of the combination of atoms into molecular groups; and the solution of the one will be the solution of the other.

The contention between the two modes of explanation seems to be capable of more easy decision empirically. It might be recommended to determine the densities of vapours not only by weighing, but also indirectly in the way proposed by Leslie and Bunsen, viz. by observation of their speeds of effusion at different temperatures and under different pressures. Perhaps, too, transpiration- and thermal-measurements may give help in the determination.

At present we shall look on both explanations as equally entitled to consideration, and must consider the probability to be that both circumstances, as discussed in §§ 48–50, work together to cause actual gases and vapours to deviate in their behaviour from the ideal laws.

# CHAPTER V

## *MOLECULAR AND ATOMIC ENERGY*

### 52. Dulong and Petit's Law for Gases

THE theories of Clausius and Maxwell, developed in Chapters II. and III., form, in the first place, a kind of molecular mechanics; but as heat is nothing else but the mechanical motion of molecules, these theories are entitled to form the basis of the laws of heat no less than of those of mechanics. One of the immediate conclusions from it is a theorem that exhibits a marked analogy with the law respecting the specific heats of solid bodies, which was discovered by Dulong and Petit.

If the temperature of a gas rises by 1 degree, the kinetic energy (§§ 14, 16)

$$E = \tfrac{1}{2}mG^2 = \tfrac{1}{2}m\mathfrak{G}^2(1 + a\vartheta),$$

which its molecules possess on the average, increases by

$$\tfrac{1}{2}m\mathfrak{G}^2 a,$$

a magnitude which, by what has gone before, is the same for all gases.

On the other hand, the law which Dulong and Petit discovered for the specific heats of solid bodies may, as is well known, be expressed in the form that, in order to heat chemically different bodies to the same extent, the same amount of heat must be communicated to every atom; and for this we generally say more shortly that the atomic heat of all bodies is the same.

If we remember that on our theory heat and energy are identical, the analogy we have mentioned at once comes into view. *By a rise of temperature the energy of each* ATOM *in the* SOLID *state increases by the same amount*, and, on the contrary, *in the* GASEOUS *state the kinetic energy of each* MOLECULE *increases by the same amount.*

The analogy of the two laws, which, by the bye, can claim only an approximate and limited validity, does not, however, entitle us to consider them identical, and to take as the specific heat the magnitude

$$\frac{1}{2}m\mathfrak{G}^2a$$

obtained above as constant for gases. In the next paragraph we shall examine its meaning more closely.

## 53. Ratio of the Molecular to the Total Energy

From the calculation of the mean speed of the molecules in absolute measure the value of the kinetic energy of molecular motion present in the gas is at once known. On the other hand, the value of the total energy present in the gas can be calculated from its heat-capacity and temperature, since it is equivalent to the heat contained in it. The question arises, whether the two values calculated by these different methods are in harmony with each other, and the resolution of such a doubt rests on the following considerations, which are borrowed from Clausius.

We ought not to expect the two values to be quite identical, so that the calculated kinetic energy should be the exact equivalent of the heat-energy; for the molecules, on their side, consist of atoms that are separately movable. The kinetic energy of those motions which the whole complex of atoms in a molecule together execute need therefore not be the whole energy contained in the gas, but there may, in addition to the forward motion of the molecules as they course to and fro, be other internal motions of the single atoms. The whole energy, calculated from the contained heat, may very well then be greater than the energy of molecular motion.

We find the total heat-energy contained in a gas by assuming that it has been brought into its present condition by being warmed at constant volume from the absolute zero to the temperature $\Theta$. If the volume filled by the gas is unity, and therefore the mass of the gas given by the density $\rho$, the heat needed is

$$c\rho\Theta,$$

where $c$ is the specific heat of the gas at constant volume. If $J$ is the value of the mechanical equivalent of heat, the equivalent of this amount of heat in terms of mechanical energy is

$$H = Jc\rho\Theta.$$

With this value of the whole amount of energy in unit volume of the gas we have to compare the value

$$K = \tfrac{3}{2}p,$$

which we obtained in § 16 for the kinetic energy of molecular motion contained in the same unit volume.

Since in regard to the latter magnitude we know that in correspondence with Gay-Lussac's law it increases proportionally to the absolute temperature when heat is added, we see at once that both $H$ and $K$ are proportional to the absolute temperature $\Theta$. Their ratio is therefore a constant number independent of the temperature of the gas, constant at least if the assumption founded on Regnault's observations for atmospheric air is in general true, viz. that the specific heat $c$ at constant volume does not alter with the temperature. Since also both magnitudes are proportional to the density $\rho$, we have with that supposition the proposition: *In a perfect gas the kinetic energy of the molecules stands in a constant ratio to the total energy contained in the gas.*

The formulæ given are sufficient to determine the numerical value of this ratio. But the proceeding employed by Clausius,[1] of first reducing to the same units the two magnitudes to be compared, and of giving them as nearly as possible the same form, is more to be recommended. This was done by Clausius in the same way as J. R. Mayer[2] determined the value of the mechanical equivalent, by finding the thermal equivalent for the energy contained in a gas in the form of pressure.

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[1] *Pogg. Ann.* c. 1857, p. 377; *Abhandl. über Wärmetheorie*, 2. Abth. p. 256; *Mech. Wärmetheorie*, iii. 1889–91, p. 35; transl. *Phil. Mag.* [4] xiv. 1857, p. 108.

[2] *Ann. Chem. Pharm.* xlii. 1842, p. 239; *Mechanik der Wärme*, 1867, p. 28.

In order to heat to the temperature $\Theta$ under constant pressure a mass of gas $\rho$, which at constant volume needs an amount of heat

$$c\rho\Theta$$

for the same rise of temperature, the greater amount of heat

$$C\rho\Theta$$

is needed, where $C$ expresses the specific heat at constant pressure. The difference between these magnitudes

$$(C-c)\rho\Theta$$

serves therefore only to increase the volume, and thereby maintain the pressure constant.

We find the mathematical expression for the expenditure of energy needed for any action, or, more shortly, for the work done, by multiplying the force by the distance through which it has been overcome. In our case the force on unit area is given by the pressure $p$, and the action consists in overcoming this pressure through the whole extent of the volume $v$, and, since the latter is assumed equal to unity, the work done is

$$pv=p.$$

The production of this work, the initial value of which was zero at the temperature of absolute zero, is equivalent to the above heat, as is expressed by the equation

$$p=J(C-c)\rho\Theta,$$

$J$ here again representing the mechanical equivalent.

If we apply this formula, which is just the same as that employed by J. R. Mayer for his calculation of $J$, to the value of the molecular and total energies $K$ and $H$, we get the equation found by Clausius, viz.:—

$$\frac{K}{H}=\frac{3}{2}\frac{C-c}{c},$$

which shows that the ratio of the two energies is determined by that of the two specific heats.

In this form the proof is bound up, as was before mentioned, with the assumption that the gas obeys the ideal gaseous laws, and especially that its specific heat $c$ at constant volume does not alter with the temperature. We can, however, easily free ourselves from this assumption and establish a more general formula, which serves also for the case wherein the specific heat does vary with the temperature.

If $\Theta$, $\Theta_0$ are two temperatures between which the value of the specific heat may be taken constant, the formula

$$H - H_0 = Jc\rho(\Theta - \Theta_0)$$

gives the whole amount of energy which must be added to unit volume of the gas to heat it from $\Theta_0$ to $\Theta$ without expansion. The kinetic energy of the molecular motion thereby simultaneously increases by

$$K - K_0 = \tfrac{3}{2}(p - p_0)$$

where $p - p_0$ is the resulting increase of pressure. Since for this change of pressure the relation

$$p - p_0 = J(C - c)\rho(\Theta - \Theta_0)$$

holds good, we have the more general formula

$$\frac{K - K_0}{H - H_0} = \frac{3}{2}\frac{C - c}{c},$$

the interpretation of which is quite similar.

## 54. Monatomic Molecules

To prove whether or not this theoretical formula corresponds to the truth, we may apply it to the special case of a gas whose molecules consist each of a single atom. To this class of gases, which we may call *monatomic,* if we may use this word in a different sense from the term *single-valued,* belong the vapours of mercury, cadmium, and perhaps zinc. For these monatomic vapours the possibility of assuming proper motions of the atoms, in addition to the motion of the molecules, falls to the ground; we shall therefore have to suppose that in these vapours the kinetic energy $K$ is identical with the total energy $H$, provided that, like gases, they may be considered free from cohesion.

For this class of bodies, therefore, $K - K_0 = H - H_0$, and thus

$$\frac{C - c}{c} = \frac{2}{3},$$

or, if this assumption is correct, the ratio of the two specific heats must be

$$\frac{C}{c} = \frac{5}{3}.$$

Led by this consideration Kundt and Warburg[1] have submitted mercury vapour to an investigation, the result of which completely confirmed the exactness of the theoretical formula. They determined the ratio of the specific heats from the speed of sound, which can be found from the wave-length of a tone. By comparing the wave-lengths of the same tone both in air and mercury vapour they found that the ratio of the specific heats of mercury vapour is really

$$\frac{C}{c} = 1{\cdot}67,$$

if after Röntgen's[2] determination the value of this ratio for atmospheric air is taken as

$$\frac{C}{c} = 1{\cdot}405.$$

Exactly the same behaviour has been also observed in the case of the newly discovered gases, argon and helium,[3] and the conclusion has therefore been drawn that, in their case too, each molecule consists of but a single atom.

Since this fact, that $C/c = 1\frac{2}{3}$ for a monatomic gas, is established by observation, we must assume that the theoretical hypothesis which led to its discovery corresponds also to the truth. In mercury vapour, therefore, and in the other monatomic gases, $H = K$, that is, there is no other nergy of any kind but that of the progressive motion of the molecules.

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[1] *Ber. der deutsch. Chem. Ges.* Berlin viii. 1875, p. 945; *Pogg. Ann.* clvii. 1876, p. 353.

[2] *Pogg. Ann.* cxlviii. 1873, p. 580.

[3] Rayleigh and Ramsay, *Proc. Roy. Soc.* lvii. 1895, pp. 282, 286; Ramsay, *Gases of the Atmosphere*, London 1896.

This excludes the idea that a rotation of the molecules about their centroids can occur; or, at least, if such a rotation be present, it cannot be altered by addition of heat; for, though we need not put $H = K$, we must at least put $H - H_0 = K - K_0$. The rotation of the particles has therefore to be independent of their rectilinear motion, and has not to be altered by collision between two particles. This is difficult to understand if the laws of elastic collision are to hold good for the collisions of atoms. We may not therefore figure the atoms as small elastic bodies occupying spaces, like spheres for instance, but as vanishingly small massive points, if we do not make other assumptions as to their nature, to which we shall return in Chapter X., §§ 123 and 124.

That monatomic gaseous molecules also may be capable of oscillatory motions in their interior we may look upon as probable, since in their spectra whole series of different lines are found. But these motions, as we may assume in accordance with E. Wiedemann's[1] observations, require so small an expenditure of energy that its amount does not come at all into account in comparison with the kinetic energy of the molecular motion.

Hence monatomic molecules need in no way be rigid massive points; it is only necessary that they should be very small particles in whose interior only such motions can come into play as demand but very little energy. It therefore does not appear impossible that the ratio $C/c = 1{\cdot}67$ should be found in the case of chemically compound molecules also, if the connection of the atoms is so firm that internal motions are excluded.

## 55. Polyatomic Molecules

In the case of a gas whose molecules are made up of several atoms, the ratio of the kinetic to total energy, $K : H$, is indeed not directly known; but in spite of this we can here too test by observation the correctness of the theory to a certain extent. For, since $K$, as a part of $H$, is not greater than $H$, but can at most be equal to $H$, our formula, which can be put in the form

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[1] *Wied. Ann.* 1889, xxxvii. pp. 241, 248. Comp. § 123.

$$\frac{C}{c} = 1 + \frac{2}{3}\frac{K}{H},$$

or, more generally,

$$\frac{C}{c} = 1 + \frac{2}{3}\frac{K - K_0}{H - H_0},$$

gives limits for the values which the ratio of the two specific heats can have; thus the formula gives

$$1 < \frac{C}{c} < 1 + \frac{2}{3},$$

or the value of the ratio must in all cases lie between 1 and $\frac{5}{3}$.

Since the experimental determinations of this ratio mentioned further on confirm this theoretically deduced law without exception, we may consider ourselves justified in using the formula

$$\frac{K}{H} = \frac{3}{2}\frac{C - c}{c}$$

in the reverse way, and in calculating for different gases the ratio of the kinetic energy $K$ of the molecules to the whole heat-energy $H$ from the values of the ratio of the two specific heats that have been determined by observation. At least, for a gas whose specific heat is not variable with the temperature the sufficiency of this formula instead of the more general one

$$\frac{K - K_0}{H - H_0} = \frac{3}{2}\frac{C - c}{c}$$

will not be contested; for other gases the simpler formula will give values that are very approximately correct.

The value of the ratio in which the two specific heats stand to each other has indeed been experimentally determined for a tolerably large number of gases, though unfortunately not in all cases with such certainty as for our purpose is desirable. For since the formula does not contain only the ratio, but also the difference of these magnitudes, the uncertainty of the values calculated by means of this formula will become still greater.

For atmospheric air we have to take for this ratio the value

$$\frac{C}{c} = 1{\cdot}405\,;$$

this we obtain from Dulong's[1] and Masson's[2] observations on the speed of sound,[3] if we apply a correction[4] that according to the newer measures is necessary; and this value is in harmony not only with Wüllner's[5] experiments by the same method, but also with Röntgen's[6] determinations by Desormes and Clément's[7] procedure, and with P. A. Müller's[8] observations by Assmann's[9] method.

From this value we obtain by the formula

$$\frac{K}{H} = \frac{3}{2}\left(\frac{C}{c} - 1\right) = 0{\cdot}608\,;$$

the energy $K$ therefore of the molecular motion in atmospheric air stands to the whole energy $H$ contained in the gas in about the ratio 3 : 5. Thence it follows that the two parts into which we may break up the whole energy $H$, viz. the internal energy $H - K$ of the molecule (which we may distinguish as the *atomic energy*) and the energy $K$ of its progressive motion, must bear to each other nearly the ratio 2 : 3; or, more exactly, we have

$$\frac{H - K}{K} = 0{\cdot}646.$$

The values of $H$ and $K$ have hitherto been referred to unit volume. If, however, we are concerned with only the *ratio* of their values, it is unnecessary to refer them to unit volume, and we may refer their values to any arbitrary volume, as, for instance, the molecular volume. Hence if, as in § 21* of the Mathematical Appendices, we denote the mean energy of forward motion of *a single* molecule by $E$, and the mean value of its internal atomic energy by $\mathfrak{E}$, the ratio of these two magnitudes is equal to that calculated above, viz.

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[1] *Ann. Chim. Phys.* xli. 1829, p. 113; *Pogg. Ann.* xvi. p. 438.

[2] *Ibid.* [3] liii. 1858, p. 257.

[3] Compare § 36.

[4] Wüllner's *Lehrbuch d. Experimentalphysik*, 4. Aufl. 1885, iii. p. 522.

[5] *Wied. Ann.* iv. 1878, p. 321.

[6] *Pogg. Ann.* cxlviii. 1873, p. 580.

[7] *Journ. de Phys.* lxxxix. 1819, pp. 321, 428.

[8] *Inaug. Diss.* Breslau 1882; *Wied. Ann.* xviii. 1883, p. 94.

[9] *Pogg. Ann.* lxxxv. 1852, p. 1.

$$\frac{\mathfrak{E}}{E}=\frac{H-K}{K}.$$

This somewhat altered conception allows us to compare the mean amount of energy $\mathfrak{e}$ possessed by a single atom with the molecular energy. For if the number of atoms in the molecule is $\mathfrak{n}$, then the desired mean value is

$$\mathfrak{e}=\frac{\mathfrak{E}}{\mathfrak{n}}.$$

Since air is not a chemical compound of unchangeable composition it is not, strictly speaking, allowable to apply this formula to it. But since its components, nitrogen and oxygen, have the common property of possessing two atoms in a molecule, we may also for air put $\mathfrak{n}=2$, and obtain

$$\frac{\mathfrak{E}}{E}=0{\cdot}646, \quad \frac{\mathfrak{e}}{E}=0{\cdot}323.$$

The energy $\mathfrak{e}$ of an atom is thus considerably smaller than the energy $E$ of progressive motion of a molecule of air. This ratio is in agreement also with that for most other gases, as the following table shows.

The first column of figures contains the observed values of the ratio of the specific heats for a series of gases and vapours. The observations of Dulong ($D$) and Masson ($Mn$) are given according to Wüllner's corrected calculation; also in Wüllner's ($W$) determinations the corrections later applied by Strecker and Wüllner are taken into account.[1] In addition to these I have taken the observations of Röntgen ($R$), P. A. Müller ($Mr$), Strecker ($S$),[2] de Lucchi ($L$),[3] Martini ($Mi$),[4] Maneuvrier and Fournier

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[1] Wüllner's *Lehrbuch*, 4. Aufl. 1885, iii. p. 522.

[2] *Inaug. Diss.* Strassburg; *Wied. Ann.* xiii. 1881, p. 20; xvii. 1882, p. 85.

[3] *Nuovo Cimento* [3] xi. 1882, p. 11; *Exner's Rep.* xix. 1883, p. 249.

[4] *Atti del Ist. Ven.* [5] vii. 1880–1, p. 491; Landolt and Börnstein's *Tables*, 2 ed. p. 340, tab. 137.

(*MF*),[1] Lummer and Pringsheim (*LP*),[2] Capstick (*Ck*),[3] and also those of Cazin (*C*),[4] though these may be less exact. From these observed values are then calculated the values of the ratios $K : H$, $\mathfrak{E} : E$, and $\mathfrak{e} : E$.

*Molecular and Atomic Energy*

| Gas | Molecular Formula | $\frac{C}{c}$ | Observer | $\frac{K}{H}$ | $\frac{\mathfrak{E}}{E}$ | $\frac{\mathfrak{e}}{E}$ |
|---|---|---|---|---|---|---|
| Air | | 1·403 | LP | 0·604 | 0·656 | 0·328 |
| Oxygen | $O_2$ | 1·398 | ,, | 0·597 | 0·676 | 0·338 |
| | | 1·402 | D | 0·603 | 0·658 | 0·329 |
| | | 1·403 | Mr | 0·604 | 0·656 | 0·328 |
| | | 1·405 | Mn | 0·607 | 0·646 | 0·323 |
| | | 1·410 | C | 0·615 | 0·626 | 0·313 |
| Nitrogen | $N_2$ | 1·405 | Mn | 0·607 | 0·646 | 0·323 |
| | | 1·410 | C | 0·615 | 0·626 | 0·313 |
| Hydrogen | $H_2$ | 1·394 | D | 0·591 | 0·692 | 0·346 |
| | | 1·405 | Mn | 0·607 | 0·646 | 0·323 |
| | | 1·408 | LP | 0·613 | 0·632 | 0·316 |
| | | 1·410 | C | 0·615 | 0·626 | 0·313 |
| Carbon monoxide 0° | CO | 1·403 | W | 0·605 | 0·653 | 0·327 |
| 100° | | 1·397 | ,, | 0·595 | 0·679 | 0·340 |
| | | 1·410 | C | 0·615 | 0·626 | 0·313 |
| | | 1·410 | D | 0·615 | 0·626 | 0·313 |
| | | 1·413 | Mn | 0·619 | 0·614 | 0·307 |
| Nitric oxide | NO | 1·394 | ,, | 0·591 | 0·692 | 0·346 |
| Hydrogen chloride | HCl | 1·392 | ,, | 0·586 | 0·706 | 0·353 |
| | | 1·394 | S | 0·591 | 0·692 | 0·346 |
| | | 1·398 | Mr | 0·597 | 0·675 | 0·338 |
| Hydrogen bromide | HBr | 1·365 | ,, | 0·547 | 0·828 | 0·414 |
| | | 1·431 | S | 0·646 | 0·547 | 0·273 |
| Hydrogen iodide | HI | 1·397 | ,, | 0·595 | 0·679 | 0·340 |
| Bromine iodide | BrI | 1·33 | ,, | 0·495 | 1·02 | 0·51 |
| Chlorine iodide | ClI | 1·317 | ,, | 0·475 | 1·103 | 0·551 |
| Chlorine | $Cl_2$ | 1·323 | ,, | 0·484 | 1·064 | 0·532 |
| | | 1·336 | Mi | 0·504 | 0·984 | 0·492 |
| Bromine | $Br_2$ | 1·293 | S | 0·439 | 1·275 | 0·638 |
| Iodine | $I_2$ | 1·294 | ,, | 0·441 | 1·268 | 0·634 |
| Carbonic acid | $CO_2$ | 1·265 | Mr | 0·398 | 1·513 | 0·504 |
| | | 1·277 | Mn | 0·415 | 1·407 | 0·469 |
| | | 1·291 | C | 0·436 | 1·291 | 0·430 |
| | | 1·292 | L | 0·438 | 1·283 | 0·428 |
| | | 1·300 | LP | 0·449 | 1·226 | 0·409 |
| | | 1·305 | R | 0·457 | 1·186 | 0·395 |
| | | 1·308 | Ck | 0·462 | 1·164 | 0·388 |
| 0° | | 1·311 | W | 0·467 | 1·141 | 0·380 |
| 100° | | 1·284 | ,, | 0·426 | 1·345 | 0·448 |
| | | 1·326 | D | 0·489 | 1·045 | 0·348 |

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[1] *Comptes rendus*, cxxiv. 1898, p. 183.

[2] *Wied. Ann.* lxiv. 1898, p. 555. *Rep. Brit. Ass.* 1894, p. 565.

[3] *Proc. Roy. Soc.* lvii. 1895, p. 322.

[4] *Ann. Chim. Phys.* [3] lxvi. 1862, p. 206.

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| Gas | Molecular Formula | $C/c$ | Observer | $K/H$ | $\mathfrak{E}/E$ | $\mathfrak{e}/E$ |
|---|---|---|---|---|---|---|
| Nitrous oxide | $N_2O$ | 1·270 | Mn | 0·405 | 1·469 | 0·490 |
|  |  | 1·285 | C | 0·427 | 1·339 | 0·446 |
| 0° |  | 1·311 | W | 0·466 | 1·146 | 0·382 |
| 100° |  | 1·275 | ,, | 0·412 | 1·429 | 0·476 |
|  |  | 1·331 | D | 0·496 | 1·014 | 0·338 |
| Water vapour 103° | $H_2O$ | 1·277 | L | 0·415 | 1·407 | 0·469 |
| Sulphur dioxide | $SO_2$ | 1·248 | Mn | 0·372 | 1·689 | 0·563 |
|  |  | 1·256 | Mr | 0·384 | 1·602 | 0·534 |
|  |  | 1·262 | C | 0·393 | 1·545 | 0·515 |
| Hydrogen sulphide | $H_2S$ | 1·258 | Mn | 0·387 | 1·584 | 0·528 |
|  |  | 1·276 | Mr | 0·414 | 1·415 | 0·472 |
|  |  | 1·340 | Ck | 0·510 | 1·961 | 0·654 |
| Carbon disulphide | $CS_2$ | 1·189 | Mr | 0·283 | 2·527 | 0·842 |
|  |  | 1·239 | Ck | 0·359 | 1·789 | 0·596 |
| Acetylene | $C_2H_2$ | 1·26 | MF | 0·39 | 1·56 | 0·39 |
| Ammonia | $NH_3$ | 1·262 | Mr | 0·393 | 1·543 | 0·386 |
|  |  | 1·304 | Mn | 0·456 | 1·193 | 0·298 |
| 0° |  | 1·317 | W | 0·476 | 1·102 | 0·275 |
| 100° |  | 1·279 | ,, | 0·419 | 1·389 | 0·347 |
|  |  | 1·328 | C | 0·472 | 1·119 | 0·280 |
| Phosphorus 300° | $P_4$ | 1·175 | L | 0·262 | 2·81 | 0·702 |
| Marsh gas | $CH_4$ | 1·316 | Mr | 0·474 | 1·110 | 0·222 |
|  |  | 1·319 | Mn | 0·478 | 1·090 | 0·218 |
| Methyl chloride | $CH_3Cl$ | 1·199 | Mr | 0·299 | 2·35 | 0·470 |
| Methylene chloride | $CH_2Cl_2$ | 1·119 | ,, | 0·179 | 4·59 | 0·92 |
|  |  | 1·219 | Ck | 0·329 | 2·044 | 0·409 |
| Chloroform | $CHCl_3$ | 1·110 | Mr | 0·165 | 5·06 | 1·01 |
|  |  | 1·154 | Ck | 0·231 | 3·33 | 0·67 |
| Carbon tetrachloride | $CCl_4$ | 1·130 | ,, | 0·195 | 4·13 | 0·83 |
| Silicon tetrachloride | $SiCl_4$ | 1·129 | ,, | 0·194 | 4·17 | 0·83 |
| Ethylene | $C_2H_4$ | 1·228 | D | 0·342 | 1·92 | 0·321 |
|  |  | 1·264 | Ck | 0·396 | 1·525 | 0·254 |
| 0° |  | 1·245 | W | 0·368 | 1·72 | 0·286 |
| 100° |  | 1·189 | ,, | 0·283 | 2·53 | 0·422 |
|  |  | 1·243 | Mr | 0·364 | 1·74 | 0·291 |
|  |  | 1·257 | C | 0·385 | 1·59 | 0·266 |
|  |  | 1·260 | Mn | 0·390 | 1·56 | 0·261 |
| Vinyl bromide | $C_2H_3Br$ | 1·198 | Ck | 0·297 | 2·37 | 0·39 |
| Aldehyde | $C_2H_4O$ | 1·145 | Mr | 0·218 | 3·58 | 0·51 |
| Ethyl chloride | $C_2H_5Cl$ | 1·126 | ,, | 0·189 | 4·30 | 0·54 |
| Ethylene chloride | $C_2H_4Cl_2$ | 1·085 | ,, | 0·128 | 6·81 | 0·85 |
|  |  | 1·137 | Ck | 0·206 | 3·87 | 0·48 |
| Ethylidene chloride | $C_2H_4Cl_2$ | 1·134 | ,, | 0·201 | 3·98 | 0·50 |
| Methyl chloroform | $C_2H_3Cl_3$ | 1·037 | Mr | 0·056 | 16·9 | 2·12 |
| Methyl ether 6° | $C_2H_6O$ | 1·107 | ,, | 0·161 | 5·2 | 0·58 |
| 30° |  | 1·113 | ,, | 0·169 | 4·9 | 0·55 |
| Allyl chloride | $C_3H_5Cl$ | 1·137 | Ck | 0·206 | 3·87 | 0·43 |
| Allyl bromide | $C_3H_5Br$ | 1·145 | ,, | 0·218 | 3·58 | 0·51 |
| Ethyl formate | $C_3H_6O_2$ | 1·124 | ,, | 0·186 | 4·38 | 0·40 |
| Methyl acetate | $C_3H_6O_2$ | 1·137 | ,, | 0·206 | 3·87 | 0·35 |
| Methylal 13° | $C_3H_8O_2$ | 1·065 | Mr | 0·097 | 9·3 | 0·71 |
| 22° |  | 1·075 | ,, | 0·112 | 7·9 | 0·61 |
| 40° |  | 1·094 | ,, | 0·141 | 6·1 | 0·47 |
| Ethyl ether | $C_4H_{10}O$ | 1·029 | ,, | 0·043 | 22·2 | 1·5 |

## 56. Approximate Calculation of the Atomic Energy in Polyatomic Molecules

A further series of approximately correct values of these ratios can be obtained by a theoretical method which has been used by Sadi Carnot[1] to calculate the values of the specific heat at constant volume from the observed values of the specific heat at constant pressure.

To explain this method we introduce the values of the specific heats $\Gamma$, $\gamma$, which are referred to unit volume, instead of $C$, $c$, which refer to unit mass; these are given by

$$\Gamma = C\rho, \quad \gamma = c\rho,$$

where $\rho$ is the density of the gas referred to that of water as unity. Then for the ratio of the kinetic energy of the molecules to their whole energy we have the formula

$$\frac{K}{H} = \frac{3}{2} \frac{\Gamma - \gamma}{\gamma}.$$

This new form of the formula possesses an advantage when we take account of a law discovered by Carnot, which can be directly deduced from the formula

$$p = J(C - c)\rho\Theta$$

developed in § 53. If we write it in the form

$$p = J(\Gamma - \gamma)\Theta$$

it contains only two constants, the mechanical equivalent $J$ and the difference $\Gamma - \gamma$; of these only the latter can depend on the nature of the gas used in the experiment. But considering two different gases under equal pressures and at the same temperature, we see that *the difference* $\Gamma - \gamma$ *of the two specific heats referred to unit volume has the same value for all gases.*

It follows for our purpose, from this law, that the value of the ratio of $K$ to $H$ in different gases is inversely proportional to the specific heat $\gamma$ of unit volume of the gas at constant volume. Hence the ratios for other gases could easily be calculated from the known value of the ratio for any one gas if their specific heats at constant volume were known.

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[1] *Réflexions sur la Puissance Motrice du Feu,* Paris 1824. Reprinted in *Ann. Sci. de l'École Norm. Supér.* [2] i. 1872, p. 393. Translated into English by Professor Thurston, London 1890.

But the specific heat at constant volume is with much greater difficulty accessible to observation and measurement than the specific heat at constant pressure. On this ground no direct determinations of the former have been made.[1] But their values may be calculated from the measured values of the latter by means of the law just given, which is expressed by the last formula. Since this formula and law are strictly exact only for perfect gases, the calculation can indeed be admitted without hesitation only for such gases as have no cohesion and strictly obey Boyle's law. For other gases and vapours this calculation can only supply numbers which, at most, can claim to be approximately correct estimations.

Still more doubtful becomes the interpretation of this theoretical calculation if it is necessary to employ values of the density which are not actually observed but are theoretically deduced on the assumption of Boyle's and Gay-Lussac's laws or of Avogadro's law.

Finally, as a further cause that makes the values so calculated uncertain, must be added the circumstance observed by Regnault,[2] E. Wiedemann,[3] Winkelmann,[4] and Wüllner,[5] that the specific heat of many gases and vapours is variable in a high degree with the temperature. This is especially the case, according to an observation made by F. Weber,[6] with those compounds which contain carbon.

With these reservations the values of the specific heat

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[1] [Dr. Joly's direct determinations by means of his steam-calorimeter must not be ignored. See *Phil. Trans.* clxxxii. 1891, p. 73; clxxxv. 1894, pp. 943, 961.—Tr.]

[2] *Mém. de l'Acad. de Paris*, xxvi.

[3] *Habilitationsschrift*, Leipzig 1875; *Pogg. Ann.* clvii. 1876, p. 1.

[4] *Pogg. Ann.* clix. 1876, p. 177.

[5] *Wied. Ann.* iv. 1878, p. 321.

[6] *Hohenheimer Programm*, Stuttgart 1874, p. 82; *Pogg. Ann.* cliv. 1875, p. 580.

$\gamma$, which I have borrowed from a table calculated by Clausius[1] from Regnault's observations and displayed in the annexed table, are to be taken; and the values of the ratios in the last three columns, which I have deduced from them, must be similarly judged.

| Gas | Molecular Formula | $\mathfrak{n}$ | $\gamma$ | $\frac{K}{H}$ | $\frac{\mathfrak{E}}{E}$ | $\frac{\mathfrak{e}}{E}$ |
|---|---|---|---|---|---|---|
| Air | | | 1 | 0·615 | 0·63 | |
| Hydrogen chloride | $HCl$ | 2 | 0·975 | 0·631 | 0·58 | 0·29 |
| Hydrogen | $H_2$ | 2 | 0·990 | 0·621 | 0·61 | 0·30 |
| Nitrogen | $N_2$ | 2 | 0·996 | 0·617 | 0·62 | 0·31 |
| Carbon monoxide | $CO$ | 2 | 0·997 | 0·617 | 0·62 | 0·31 |
| Oxygen | $O_2$ | 2 | 1·018 | 0·606 | 0·65 | 0·33 |
| Nitric oxide | $NO$ | 2 | 1·018 | 0·606 | 0·65 | 0·33 |
| Chlorine | $Cl_2$ | 2 | 1·350 | 0·456 | 1·19 | 0·60 |
| Bromine | $Br_2$ | 2 | 1·395 | 0·440 | 1·27 | 0·63 |
| Hydrogen sulphide | $H_2S$ | 3 | 1·29 | 0·477 | 1·10 | 0·37 |
| Water | $H_2O$ | 3 | 1·36 | 0·452 | 1·21 | 0·40 |
| Carbonic acid | $CO_2$ | 3 | 1·55 | 0·397 | 1·52 | 0·51 |
| Sulphur dioxide | $SO_2$ | 3 | 1·62 | 0·380 | 1·63 | 0·54 |
| Nitrous oxide | $N_2O$ | 3 | 1·64 | 0·375 | 1·67 | 0·56 |
| Carbon disulphide | $CS_2$ | 3 | 2·04 | 0·301 | 2·32 | 0·77 |
| Ammonia | $NH_3$ | 4 | 1·37 | 0·449 | 1·23 | 0·31 |
| Phosphorus trichloride | $PCl_3$ | 4 | 3·39 | 0·181 | 4·51 | 1·13 |
| Arsenic trichloride | $AsCl_3$ | 4 | 3·77 | 0·163 | 5·13 | 1·28 |
| Marsh gas | $CH_4$ | 5 | 1·54 | 0·399 | 1·50 | 0·30 |
| Chloroform | $CHCl_3$ | 5 | 3·43 | 0·179 | 4·58 | 0·92 |
| Silicon tetrachloride | $SiCl_4$ | 5 | 4·21 | 0·146 | 5·85 | 1·17 |
| Tin tetrachloride | $SnCl_4$ | 5 | 4·59 | 0·134 | 6·46 | 1·29 |
| Titanium tetrachloride | $TiCl_4$ | 5 | 4·67 | 0·132 | 6·59 | 1·32 |
| Ethylene | $C_2H_4$ | 6 | 2·06 | 0·299 | 2·35 | 0·39 |
| Methyl alcohol | $CH_4O$ | 6 | 2·60 | 0·237 | 3·23 | 0·54 |
| Ethyl chloride | $C_2H_5Cl$ | 8 | 3·21 | 0·192 | 4·21 | 0·53 |
| Ethyl bromide | $C_2H_5Br$ | 8 | 3·76 | 0·164 | 5·11 | 0·64 |
| Ethylene chloride | $C_2H_4Cl_2$ | 8 | 4·24 | 0·145 | 5·90 | 0·74 |
| Alcohol | $C_2H_6O$ | 9 | 3·87 | 0·159 | 5·29 | 0·59 |
| Acetone | $C_3H_6O$ | 10 | 4·50 | 0·137 | 6·32 | 0·63 |
| Benzol | $C_6H_6$ | 12 | 5·60 | 0·110 | 8·11 | 0·68 |
| Acetic ether | $C_4H_8O_2$ | 14 | 6·82 | 0·090 | 10·09 | 0·72 |
| Ether | $C_4H_{10}O$ | 15 | 6·87 | 0·090 | 10·17 | 0·68 |
| Sulphuric ether | $C_4H_{10}S$ | 15 | 6·99 | 0·088 | 10·36 | 0·69 |
| Oil of turpentine | $C_{10}H_{16}$ | 26 | 13·71 | 0·045 | 21·29 | 0·82 |

In addition to the values of the ratio of the kinetic energy $K$ of the molecules to the whole heat-energy $H$, this table also contains, like the former one, the values of the ratios of the mean energy $\mathfrak{E}$ of all the $\mathfrak{n}$ atoms of a molecule and of the mean value $\mathfrak{e}$ for a single atom to the energy of translatory motion $E$ of the molecule. The values of this last ratio, which are placed in the last column, are in nearly all cases less than 1, and, indeed, are in general less than $\frac{1}{2}$. The number of exceptions, including perhaps ethyl ether[1] and possibly seven[1] chlorine compounds, is so small that we shall be inclined to consider the rule, that *in gases with polyatomic molecules the mean energy of an atom is smaller than the translatory energy of a molecule*, to be a veritable law of nature, which, like Boyle's and the other laws of gases, admits exceptions under certain circumstances.

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[1] *Ann. Chem. Pharm.* cxviii. 1861, p. 106; *Abhandl. ü. Wärmetheorie*, 1. Abth. 1864, p. 296; 2nd ed. 1876, p. 62; 3rd ed. 1887, p. 62.

The possible grounds for such exceptions will appear from the following considerations.

## 57. Dissociation and Disgregation

By our theory and by experiment, so far as the theory has up to the present been confirmed by observation, the molecular energy $E$ consists only in that of the linear to-and-fro motion of the molecules, that is, in *kinetic energy*, or, in the older nomenclature, in *vis viva*. We may not, however, assert this of the energy $\mathfrak{E}$ of the atoms nor of the mean energy $\mathfrak{e}$ of a single atom. For the atoms do not move freely like the molecules, which in the gaseous state exert no cohesion towards each other, but they are bound to each other by chemical affinity, and are, consequently, constrained to a certain extent in their motion. The energy of the atoms, therefore, does not consist, as that of the molecules, entirely in kinetic energy, but also in the *potential energy of the affinity* which holds the atoms together; the magnitude $\mathfrak{E}$ is the sum of the amounts of both kinds of energy which are present within the molecule, or, according to Leibniz's terminology, it is the sum of the *vis viva* and *vis mortua* of the components of the molecule. In the same way the mean energy $\mathfrak{e}$ of an atom is made up of its kinetic energy and its share of the potential energy of the chemical forces of affinity.

From this it first of all follows that we are not entitled to infer the magnitude of the speed of the atoms from the calculated values of $\mathfrak{e}$ as we were able to deduce the speed of translatory motion of the molecules from the molecular energy $E$. It would rather be allowable to estimate the strength of chemical affinity from the atomic energy $\mathfrak{e}$.

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[1] Refer also to the table of § 55.

But from what has been said regarding the character of the atomic energy we further draw this as a necessary conclusion, that an atom cannot, like a molecule, attain any speed we choose. A great speed exceeding a certain limit would be able to tear the atom from its combination with the others, and such a freed atom would then move on in straight lines free from external forces like an independent molecule, and its energy, therefore, which till then formed a part of the atomic energy, would go to increase the molecular energy $E$. Herein lies an evident ground for the view that the mean energy $\mathfrak{e}$ of an atom must be smaller than the average energy $E$ of translatory motion of the molecules.

That an atom can be actually loosened from the molecular combination by an increase in its speed cannot be doubted; to this testifies the fact of *dissociation*, that is, the phenomenon that chemical combinations can be broken up by a rise of temperature, and, therefore, by an increase in the energy of the molecules and of the atoms. With a moderate amount of heat this breaking up of molecules into single atoms does not in general occur; but among a great number of molecules there will always be some which become split up into their components in consequence either of extraordinary high speed or of collision under exceptionally favourable circumstances.

This view, first put forward by Clausius, is applicable not only to gases but also to liquids. From measurements on the conductivity of water made by F. Kohlrausch and A. Heydweiller[1] it may with great probability be assumed that even the purest water contains traces of uncombined oxygen and hydrogen.

Analogously to this partially occurring dissociation we should expect a partial chemical combination to result when two gases are mixed together at a temperature below that of normal combination or combustion. This presumption is confirmed by H. B. Dixon's[1] observations on mixtures of oxygen and hydrogen.

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[1] *Sitzungsber. d. Berl. Akad.* 1894, p. 295.

Before a complete breaking up of a compound molecule occurs the addition of heat produces a loosening of the bonds of the atoms in the molecule. In this process, which with Clausius we may term *disgregation*, the heat acts in two ways: it increases the kinetic energy of the atoms and overcomes a part of their affinity. The sum of both actions requires the expenditure of energy, which we will denote by the letter $\mathfrak{e}$.

Disgregation becomes dissociation, *i.e.* the molecules break up into their atoms, when the energy of the atomic motion is able to overcome the remaining part of the affinity.

For this to be produced the energy of motion must be at least equal in magnitude to the total amount of the energy of chemical affinity. The value therefore of the atomic energy which is attained at the temperature of commencement of complete dissociation is the mechanical measure of the maximum energy to which the chemical affinity of an atom is capable of giving rise.

## 58. Dependence of the Specific Heats on Temperature

The foregoing discussions show that the molecular and atomic energies are by no means magnitudes of the same kind. Now that we know this, it seems doubtful if both kinds of energy will increase in equal measure when the temperature rises. Hitherto we have assumed this, since the theory had given the law that the kinetic energy of the molecules bears a constant ratio to the total energy contained in a gas. The proof of this law, however, rests on the assumption, which is not in general true, that the specific heat of gases at constant volume is independent of the temperature.

We cannot well test by direct observation of the specific heat at constant volume whether this assumption is admissible. But we can with more ease and exactness determine the other specific heat, that at constant pressure, and infer from the behaviour of the one that of the other. For this the ratio of the two magnitudes need not be known if the gas in question obeys with exactness the laws of Boyle and Gay-Lussac. For the equation

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[1] *Nature*, xxxii. 1885, p. 535.

$$p = \rho\Theta \times \text{const},$$

which is the mathematical expression of these laws when, as before, $p$ represents the pressure, $\rho$ the density, and $\Theta$ the absolute temperature, in connection with the formula that we have already used several times, viz.

$$p = J(C - c)\rho\Theta,$$

in which $J$ is the mechanical equivalent of heat, immediately gives the law that the difference $C - c$ of the two specific heats is a constant independent of both pressure and temperature. This law, which was first given by S. Carnot, leads at once to the conclusion that, for those gases whose specific heat $C$ at constant pressure does not alter with the temperature and pressure, the specific heat $c$ at constant volume has also a constant magnitude.

Now Regnault[1] has experimentally shown for air and hydrogen, and Eilhard Wiedemann[2] for carbon monoxide, that the specific heat $C$ at constant pressure does not depend on the temperature. From this we may probably assume that all gases whose molecules contain two atoms will exhibit the same behaviour if they obey Boyle's and Gay-Lussac's laws exactly. In this case, therefore, there would be no doubt as to the ratio of the atomic energy $\mathfrak{E}$ to the molecular energy $E$ having a constant value.

For other gases, on the contrary, whose molecules are composed of more than two atoms, it has been observed that $C$ is by no means constant. Regnault found with carbonic acid, and E. Wiedemann with carbonic acid, ethylene, nitrous oxide, and ammonia, an unmistakable dependence of the specific heat $C$ on temperature. Lussana[1] found that for a series of gases it varies also with the pressure—increasing, in fact, with the pressure. For these gases, therefore, the specific heat $c$ at constant volume cannot be looked upon as invariable; we shall consequently have also to expect that the ratio of the atomic energy $\mathfrak{E}$ to the molecular energy $E$ depends on the temperature, and perhaps also on the pressure.

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[1] *Mém. de l'Acad. de Paris*, xxvi.

[2] *Habilitationsschrift*, Leipzig 1875 ; *Pogg. Ann.* clvii. 1876, p. 1.

This expectation is confirmed by some of the numbers given in § 55. Wüllner, as was there indicated, has found the following values for the ratio of the specific heats at 0° and 100°:—

| Gas | Value of $C/c$ at | |
|---|---|---|
| | 0° | 100° |
| Carbon monoxide . | 1·403 | 1·397 |
| Carbonic acid . . | 1·311 | 1·284 |
| Nitrous oxide . . | 1·311 | 1·275 |
| Ammonia . . . | 1·317 | 1·279 |
| Ethylene . . . | 1·245 | 1·189 |

For these gases, therefore, there appears a diminution of the ratio as the temperature rises. On the contrary, the value of the ratio of the energy of an atom $\mathfrak{e}$ to the molecular energy $E$, as calculated from these numbers, increases as the temperature rises, thus:—

| Gas | Value of $\mathfrak{e}/E$ at | |
|---|---|---|
| | 0° | 100° |
| Carbon monoxide . | 0·327 | 0·340 |
| Carbonic acid . . | 0·380 | 0·448 |
| Nitrous oxide . . | 0·382 | 0·476 |
| Ammonia . . . | 0·275 | 0·347 |
| Ethylene . . . | 0·286 | 0·422 |

For carbon monoxide, the molecule of which contains only two atoms, the variation is slight; it is of the same order of magnitude as the deviation from the laws of Boyle and Gay-Lussac. But with the other gases the variation is much greater, and the variation seems the greater the more atoms there are in the molecule.

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[1] *Nuovo Cim.* [3] 1894, xxxvi.; [4] 1895, i.; 1896, iii.; 1897, vi.; 1898, vii. *Atti del Ist. Veneto* [7] viii.

This remark leads to a simple explanation on the basis of the previous discussions upon the nature of the molecular and atomic energy. A possible cause was there indicated in the circumstance that the atomic energy is not, like the molecular energy, simply kinetic, but partly consists of the potential energy of chemical affinity, and that the latter is perhaps subject to different laws. If this is true, the variation must prove the greatest where the greatest forces of affinity come into play, and, therefore, will be the larger the more atoms are chemically combined. And this is in fact the case.

It still remains for us to explain why the ratio of the atomic energy $\epsilon$ to the molecular energy $E$ increases, and does not diminish, as the temperature rises. This fact is indeed to be explained only thus, that the so-called disgregation or loosening of the chemical bonds of the atoms combined in the molecule requires an expenditure of energy which is the greater the further it has already proceeded in consequence of increase of the temperature.

This assumption contains nothing improbable, provided that we suppose that the force of chemical affinity does not bring the atoms into direct contact, but endeavours to hold them at a certain distance from each other; they can then oscillate about their assigned positions of equilibrium, and rotate or move about in any other way. By addition of heat these motions will be accelerated, and the amplitude of the oscillations and, above all, the lengths of the paths will be increased without at first causing the atom to escape out of the range of action of the forces of affinity. For this proportionally little energy is needed. Far more energy, however, is required when the atom begins by its increased speed to break loose from the bonds of the molecule, because now the opposing chemical forces are to be overcome.

This explanation of the behaviour observed by Wüllner seems to contradict the fact that, according to the observations of P. A. Müller, some substances act exactly oppositely to the gases investigated by Wüllner. Müller found, as in the table of § 55,

| Gas | Temperature | $C/c$ | $\mathfrak{e}/E$ |
|---|---|---|---|
| Methyl ether . . | 6° | 1·107 | 0·58 |
| | 30° | 1·113 | 0·55 |
| Methylal . . . | 13° | 1·065 | 0·71 |
| | 22° | 1·075 | 0·61 |
| | 40° | 1·094 | 0·47 |

For these substances, therefore, the ratio of the specific heats does not decrease, but increases, as the temperature rises; and their atomic energy $\mathfrak{e}$ increases with the temperature not more, but less, rapidly than the molecular energy $E$.

It is, however, easy to see that we have here to do with quite different circumstances; for the two methyl compounds which Müller examined have not the same right as the five bodies examined by Wüllner to be considered gases. We can hardly assume that they obey the laws of Boyle, Gay-Lussac, and Avogadro, at least, not at the temperatures at which Müller made his observations. Deviations from these laws are in most cases to be ascribed to the heat not being sufficient to overcome the cohesion so far that a breaking up into simple molecules of the same kind is attained. In such vapours an addition of heat augments the number of molecules, and the value of the molecular energy thereby increases, and increases, indeed, more rapidly than the atomic energy. Müller's observations are therefore just as easy to interpret as those made by Wüllner.

At the present stage of our knowledge we shall have therefore to assume that the law discovered by Clausius, according to which the molecular and atomic energies should bear to each other a ratio that is always constant, holds good in its full strictness only for diatomic gaseous molecules; for other molecules, however, that ratio is variable with the temperature, and may, indeed, according to circumstances, either increase or decrease as the temperature rises.

But it can also happen that for diatomic molecules this law does not hold good. For among the gases whose molecules consist of two atoms there are several which do not obey the laws of Boyle and Avogadro with exactness; for these, then, Clausius' law cannot be exactly true. To this class of gases belongs, for instance, chlorine and many gaseous chlorine compounds.

Possibly we may also refer to this behaviour of chlorine the striking circumstance that, of the possibly eight substances for which the ratio of the atomic energy $\mathfrak{e}$ to the molecular energy $E$ was found greater than 1, seven are chlorine compounds. For these substances the temperature at which the ratio of the specific heats $C$ and $c$ has been determined will perhaps not have been high enough for a complete breaking up of the vapour into single molecules to have been attained.

The deviation exhibited by ethyl ether will be explainable in the same way. If the measurements had been made at higher temperatures, there would doubtless have been found a greater value of the ratio of $C$ to $c$, as in the case of methyl ether; and the calculation would then have given a smaller value for the ratio borne by the atomic energy $\mathfrak{e}$ to the molecular energy $E$.

The law that *in real gases the share of energy possessed by each atom of a molecule is always less than the translatory kinetic energy of the molecule* would not therefore be confuted by the eight exceptions.

## 59. Dependence of the Specific Heat on the Number of Atoms

From the foregoing remarks on the nature of atomic energy it at once follows that the total amount of atomic energy $\mathfrak{E}$ depends on the number of atoms contained in the molecule, and, indeed, must increase with this number. That such is the case is at once seen by a glance at the values of the ratio $\mathfrak{E}$ to $E$ in the sixth column of the table in § 55.

On closer examination further regularities come to view. Among them the fact is especially striking that the ratios for the gases $O_2$, $N_2$, $H_2$, CO, NO that head the table are very nearly identical; for them the whole atomic energy $\mathfrak{E}$ is to the molecular energy $E$ nearly as 2 : 3, and since all these gases have diatomatic molecules, the mean energy $\mathfrak{e}$ of an atom is to the molecular energy $E$ nearly as 1 : 3. This class of gases, therefore, possesses the really remarkable property that at equal temperatures not only are the values of their *molecular* energy equal to each other, but also those of their *atomic* energy, and, consequently, also their whole heat-energy. These bodies, therefore, obey in the gaseous state the law of Dulong and Petit, to which other substances in the solid state are subject.

Not all diatomic gases seem to follow this law equally. Even though HCl, HI, and perhaps HBr, obey it to some extent, yet BrI, ClI, $Cl_2$, $Br_2$, and $I_2$ exhibit very considerable deviations from it. But we need not on this account completely deny the validity of this law for diatomic gases. For the substances last named are rather vapours than gases, and it is therefore probable that with them the ratio of the specific heats increases with rising temperature. It is therefore not impossible that for all diatomic gases the ratios

$$\frac{C}{c} = 1{\cdot}4 \quad \text{and} \quad \frac{\mathfrak{e}}{E} = 0{\cdot}33$$

would be found if the measurements were made at such pressure and temperature that the laws of perfect gases were exactly obeyed.

For monatomic gases theory and observation agree (see § 54) in giving

$$\frac{C}{c} = 1{\cdot}67 \quad \text{and} \quad \mathfrak{e} = 0.$$

The idea is accordingly suggested that the value of the ratio of the specific heats, as also those of the different species of energy, depends, not on the material of the atoms, but on their number. The observations quoted seem also to indicate this; at least the numbers for the triatomic gases oscillate about the mean values

$$\frac{C}{c} = 1{\cdot}27 \quad \text{and} \quad \frac{\mathfrak{e}}{E} = 0{\cdot}5.$$

It has therefore also been attempted to find a general law of dependence of the ratio of the specific heats on the number of atoms in the molecule. After Boedeker[1] and Buff[2] had recognised the existence of simple relations between the ratios for different gases, Naumann[3] gave a formula which is based on the assumption that the ratio of $\mathfrak{e}$ to $E$ that has been found for diatomic gases, viz. 1 : 3, holds in general for all gases. On theoretical grounds Boltzmann[4] put forward the view that the mean energy $\mathfrak{e}$ of an atom must be equal to the kinetic energy $E$ of the molecule, but he found this assumption not confirmed by observation. Pilling[5] obtained a formula that agrees very well with measurement by starting with the hypothesis that the atoms exert on each other forces which vary inversely as the sixth power of the distance between them. Eddy[6] has made the more general assumption that the action is inversely proportional to some power of the distance; but Richarz[7] has proved by general theorems of mechanics that an assumption of this kind respecting the law of action between atoms is inadmissible, as it does not satisfy the conditions for the stability of the molecular combination. A new memoir by Staigmuller[8] on the kinetic theory of polyatomic gases must also be mentioned.

## 60. Degrees of Freedom of the Motion

In another way Maxwell[9] and Watson[10] have attempted to answer the question by taking into account the number of ways in which a system of particles is movable. In this method they have been followed by Boltzmann,[1] and then by Roiti,[2] and later also by Violi.[3] It shall be given here on account of its clearness, although very weighty objections must be raised against its admissibility.

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[1] *Die gesetzmäss. Beziehungen zw. d. Dicht. d. spec. Wärme u. d. Zusammensetzung der Gase*, Göttingen 1857; *Gött. Nachr.* 1857, p. 165; *Ann. d. Chem.* civ. 1857, p. 205.

[2] *Ann. d. Chem.* cxv. 1860, p. 301.

[3] *Ibid.* cxlii. 1867, p. 284; *Grundriss d. Thermochemie*, 1869, p. 44.

[4] *Wien. Sitzungsber.* lxiii. pt. 2, 1871, pp. 397, 417.

[5] *Ueber die Beziehungen d. Wärmecapacität der Gase zu den zwischen Atomen wirkenden Kräften*, Inaug.-Diss., Jena 1876.

[6] *Scient. Proc. Ohio Mech. Inst.* 1883, p. 26.

[7] *Wied. Ann.* xlviii. 1893, p. 476.

[8] *Ibid.* lxv. 1898, p. 655.

[9] *Nature*, xi. 1875, p. 357; *Scientific Papers*, ii. 418; *Nature*, xvi. 1877, p. 242.

[10] *Kinetic Theory of Gases.* Oxford 1876, pp. 27, 37; 2nd ed. 1893, p. 81.

We can assert with regard to a single massive point that it has a threefold freedom of movability, since its motion is determined by the values of the three components of its velocity. The above-named English physicists ascribe to it, therefore, three degrees of freedom, which Boltzmann expresses as three kinds of movability (*Beweglichkeitsarten*). A material system consisting of a multitude of particles possesses as many degrees of freedom or kinds of movability as the number of variables which must be given for the complete determination of its state of motion; if made up of atoms, therefore, a gaseous molecule has a greater number of degrees of freedom, the number depending upon that of the atoms. This mode of attacking the question is marked by simplicity and clearness, and it therefore leads to very simple results.

If heat $W$ is added to a gas whose molecules consist each of a single atom, while its volume is kept constant, the energy, which is only kinetic, will increase equally in the direction of each of the three given degrees of freedom, and thus in each by the amount $\frac{1}{3}W$ measured in heat-units. If this gas is heated at constant pressure, so as to attain the same temperature as before, there must, in addition to the heat $W$, be given to it, to overcome the external forces, a further amount of heat $W'$, which bears to $W$ the ratio 2 : 3; for in this case the ratio of the specific heats is

$$\frac{C}{c} = \frac{W + W'}{W} = \frac{5}{3},$$

whence

$$\frac{W'}{W} = \frac{2}{3}.$$

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[1] *Wien. Sitzungsber.* lxxiv. 1877, p. 553; *Pogg. Ann.* clx. 1877, p. 175; transl. *Phil. Mag.* [5] iii. 1877, p. 320.

[2] *Atti dell' Acc. dei Lincei* [3] i. 1877, p. 774; *Nuovo Cimento* [3] ii. 1877, p. 61.

[3] *Atti dell' Acc. dei Lincei* [3] vii. 1883, p. 112; *Nuovo Cimento*, xiv. 1884, p. 183.

If now a gas which possesses $\mathfrak{q}$ degrees of freedom is heated just as much, each of the $\mathfrak{q}$ degrees of freedom will require a corresponding share of heat, and therefore

$$\tfrac{1}{3}\mathfrak{q}W$$

heat-units are necessary for the heating at constant volume, if we have to consider only translatory kinetic energy. If, besides, there is other energy in question, a further amount of heat

$$\tfrac{1}{3}h\mathfrak{q}W$$

is needed, where $h$ is a constant. The whole heat, therefore, required for heating at constant volume is

$$\tfrac{1}{3}(\mathfrak{q} + h\mathfrak{q})W;$$

on the contrary, for heating at constant pressure the heat

$$\tfrac{1}{3}(\mathfrak{q} + h\mathfrak{q})W + W' = \tfrac{1}{3}(\mathfrak{q} + h\mathfrak{q} + 2)W$$

is needed. The specific heats, therefore, must be in the ratio

$$\frac{C}{c} = \frac{\mathfrak{q} + h\mathfrak{q} + 2}{\mathfrak{q} + h\mathfrak{q}} = 1 + \frac{2}{\mathfrak{q}(1 + h)},$$

where $h$ is a constant and $\mathfrak{q}$ the number of degrees of freedom and therefore an integer, the value of which is the greater the more atoms there are in a molecule.

Before this formula can be tested by experiment, the mode of dependence of $\mathfrak{q}$ on the number of atoms $\mathfrak{n}$ must be determined. In most cases, since the degree of movableness of the atoms is in general unknown, this can only be done by the aid of hypotheses; and for several cases such necessary hypotheses have been made.

Of these we shall here pursue those which Boltzmann has investigated. For monatomic molecules $\mathfrak{q} = 3$, and, since $C/c = \frac{5}{3}$,

$$h = 0.$$

If the molecules consist each of two atoms, Boltzmann puts $\mathfrak{q} = 5$, since he assumes that the atoms do not alter their distance apart, but are bound fast together; the position of a molecule is then completely given by the three coordinates of its centroid and by two angles, which determine the direction of the joining line of the two atoms. The formula therefore becomes

$$\frac{C}{c} = 1 + \frac{2}{5(1 + h)},$$

and gives the value

$$\frac{C}{c} = 1{\cdot}4,$$

—which has been found for atmospheric air and other diatomic gases—if for these gases also may be put

$$h = 0.$$

We should arrive at this same result also if we considered the molecules to be rigid bodies, shaped like any figures of revolution we like; for their place and position in space are also determined by five coordinates.

But against this Pirogoff[1] has raised the justifiable objection that a figure of revolution can rotate not only about its axis of symmetry, but also about another axis at right angles to the first as well. A figure of revolution and also a diatomic molecule would thus have more than five kinds of free movability.

In spite of this objection, we may suppose that inside a diatomic molecule no shifting of the atoms towards each other occurs when the heating is kept within the limits within which the observations have been made. For this speaks the fact that for diatomic gases—at least for atmospheric air and carbon monoxide—the value of the ratio varies with the temperature only very inconsiderably.

If, therefore, the molecules of diatomic gases behave as solid bodies, in which the parts suffer no relative motion, only such motions of the atoms as consist in a common rotation of all the atoms about their centroid can occur in addition to the translatory motion of the molecule as a whole. In monatomic molecules, as we have seen, such rotations do not also occur; in their case there is nothing but the rectilinear translatory motion of the centroid.

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[1] *Fortschr. d. Physik.* 1886, 2. Abth. p. 247.

This remark can, however, be valid only so far as the question concerns the phenomena which are conditioned by heat alone. By this is only intended to be meant that addition of heat can bring about no other motions than those named. But that other kinds of motion can be produced in the molecules and atoms of gas by other causes is shown by the spectra of incandescent gases. The motions inside a molecule, which are perceptible as light, are easily brought about by electrical or chemical forces. But simple heating in gases does not cause them to radiate red or white light like solids or liquids. Hot gases, of course, send out both dark and luminous radiation; but the radiation which they emit, purely in consequence of their being heated, is very much less than that which comes from gases in combustion; and under all circumstances gases radiate heat in much less degree than solids or liquids. With this remarkable fact the results of the kinetic theory agree most excellently.[1]

It is not for all diatomic gases that the value of the ratio of the specific heats is independent of the temperature and equal to 1·4; for many of these gases it is smaller and is variable with the temperature. This fact can be interpreted in two ways. In the first place, the constant $h$, which expresses the ratio of the energy spent on internal work to the energy of translation, need not be equal to 0 for these gases; and if it is greater than zero, the ratio of $C$ to $c$ is less than 1·4.

Another, though not essentially different, possible explanation might be found in the assumption that the number of degrees of freedom $\mathfrak{q}$ is not 5, but 6. There is, indeed, a sixth kind of movability if we drop the assumption that the two atoms of the molecule must remain at an invariable distance from each other. With the value $h = 0$, the ratio would approach the value

$$\frac{C}{c} = 1{\cdot}33,$$

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[1] R. v. Helmholtz, *Licht- und Wärmestrahlung verbrennender Gase*, 1890, p. 64.

as from the table in § 55 we see is really the case for some gases.

For gases whose molecules contain three or more atoms the number of degrees of freedom $q$ is to be taken still greater, since the structure of such a molecule cannot be imagined to be that of a figure of revolution. The position of such a figure as a triangle or tetrahedron is not completely determined when only the position of its centroid and the direction of *one* axis are given; there are thus more elements required for its determination. If, therefore, we assume $q$ to be greater than 5 or 6, the ratio of $C$ to $c$ becomes smaller, and with increasing $q$ approaches more and more the limit 1, as observation also teaches.

This theory therefore gives a satisfactory account of all the principal circumstances. In spite of this we cannot think that by it the question has been exhaustively treated. For there is a weighty objection to this theory, which H. T. Eddy[1] has pointed out. Since the bonds of the atoms by which they are bound together in the molecule allow of neither perfect freedom nor perfect fastness, it does not seem admissible simply to count the kinds of movability; the degrees of freedom cannot be introduced as all of equal value, but must be brought into the calculation differently weighted. An atom in a molecule has not the same degree of freedom of its motions as the centroid of the molecule, and a limited freedom must not be counted as a perfectly unlimited freedom.

As we shall easily see, this objection amounts to the same thing as the opinion already mentioned in § 56, that the energy of the limited motion of an atom cannot be equal to the energy of a molecule, but must be smaller—an opinion which in the first edition of this book was shown to be in accordance with experiment.

On these grounds, at the Aberdeen meeting of the British Association in 1885, a great number of prominent investigators denied, or at least threw doubt upon, the validity of

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[1] *Scient. Proc. Ohio Mech. Inst.* 1883, p. 42; *Journ. Franklin Inst.* [3] lxxxv. pp. 339, 409; *Ohio Mech. Inst.* 1883, p. 82.

Boltzmann's proposition of the equal distribution of energy among the different degrees of freedom The objection which had been raised against this theorem Crum Brown was supported by Liveing, Lord Kelvin, J. J. Thomson, Hicks, and Osborne Reynolds.[1]

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[1] *Nature*, xxxii. 1885, pp. 352, 533.

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# PART II

# THE MOLECULAR FREE PATHS AND THE PHENOMENA CONDITIONED BY THEM

# CHAPTER VI

## *MOLECULAR FREE PATHS*

### 61. Objections to the Kinetic Theory

THE theory of gases developed in the foregoing investigations has been shown to be in agreement with experimentally determined laws in a series of important points; Boyle's law and Dalton's law respecting the pressure of gases are necessary consequences of the theory, which explains also the law of effusion and justifies important laws of theoretical chemistry by furnishing Avogadro's law with a convincing foundation. In spite of this, however, its admissibility would lie open to justifiable doubts and objections if we confined the investigation to the points so far considered, and omitted to pursue the consequences of our hypothesis in other directions also.

As soon, indeed, as Krönig[1] and Clausius[2] had roused the attention of the learned world in 1857 by their first memoirs, many replies and objections were raised against the hypothesis that combated the views hitherto held. But the considerations that were urged against it, far from refuting the theory against which they were marshalled, have served but to promote its development by causing Clausius to publish the important works in which, by enlarging into a scientific system the fundamental conceptions of the theory that had frequently been brought forward before his time, he made himself the real founder of the kinetic theory of gases.

The doubts put forward by Buys-Ballot,[3] Hoppe,[4]

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[1] *Pogg. Ann.* 1856, xcix. p. 315.

[2] *Ibid.* 1857, c. p. 353.

[3] *Ibid.* 1858, ciii. p. 240.

[4] *Ibid.* 1858, civ. p. 279.

Jochmann,[1] and others related to a series of very different phenomena, which were apparently irreconcilable with the theory, but are all referable to one and the same point of the theory that is easily liable to misconception.

Starting from the hypothesis that the particles of a gas are in a state of forward motion in straight lines, we have found ourselves forced to the conclusion that, for the elasticity and pressure of a gas to be explained, these motions are executed with enormous speed. A particle of air traverses a path of more than 400 metres in a second, and a molecule of hydrogen a path even four times greater. If these paths are really traversed in a single straight line, as the hypothesis of the theory seems to require, many phenomena are at once unintelligible.

Smoke can hang in still air for a long time almost immovable like a cloud. But it would be dispersed in a moment if the air molecules tore the particles of smoke away from each other, and carried them off in all directions nearly 500 metres in a second.

Sulphuretted hydrogen, generated in the corner of a room, must at once be scented everywhere in the whole room if its molecules hastened through the room in straight lines with the speed of 409 metres per second as calculated in § 28. On the contrary, we observe that the diffusion of this and other gases proceeds with the utmost slowness.

Still more convincingly than by this objection the theory seems to be refuted by the fact that gases conduct heat very slowly. For if heat consists in that rapid motion, and if this proceeds in straight lines, it must be propagated so fast by its own agency that a rise of temperature occurring at one point of a gas would be discoverable 400 metres away in no longer than a second; it must travel, in fact, quite as fast as sound.

For the same reason it would not be conceivable that the equilibrium of temperature that exists in the earth's atmosphere, where the higher layers are much colder than the lower, could be maintained; indeed there would be all the appearance of the earth's being surrounded by such good conductors that it could not maintain a temperature in which life could exist.

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[1] *Pogg. Ann.* 1859, cviii. p. 153.

## 62. Refutation of the Objections

There would, indeed, have been no need of such a piling up of objections to bring the conviction that in a theory that has already obtained confirmation in so many points there must be some conception liable to be misunderstood.

The molecules of gas certainly move with that furious speed, and also move in nearly straight paths, but only till they strike some obstacle or collide with other particles. This, however, occurs very often—so often, indeed, that the case in which a molecule of the atmosphere enveloping us traverses a path of 400 metres without actual disturbance hardly ever occurs; but each air particle collides with some other exceedingly often, indeed many million times a second.

This remarkable behaviour, which was brought to light by a theoretical calculation carried out successfully by Clausius[1] and was confirmed by Maxwell in a theoretical[2] and experimental[3] investigation closely connected with that of Clausius, puts our theory in quite a different light. We have not to consider the rectilinear backward and forward motion of the molecules as a translatory motion, bound up with enormous change of place and proceeding within wide limits of space, but as consisting of a motion of molecules among each other, proceeding tumultuously hither and thither in straight zigzags and confined within a narrow space; the molecules thus execute such a motion that the best representation of it is that of grains of corn shaken about in a closed box.

By this explanation of the character of the molecular motion the objections that have been raised fall at once to the ground; for the supposition at the bottom of each, viz. that a particle of air can in a second reach a place distant by more than 400 metres, is not at all made in the kinetic theory.

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[1] 'Ueber die mittlere Länge der Wege u.s.w.,' *Pogg. Ann.* 1858, cv. p. 239; *Collected Works*, 2. Abth. 1867, p. 260; transl. *Phil. Mag.* [4] xvii. 1859, p. 81.

[2] *Phil. Mag.* 1860 [4] xix. p. 19; xx. p. 21.

[3] *Phil. Trans.* 1866, clvi. p. 249.

How in accordance with this we have to explain the slowness with which the diffusion of gases proceeds is clear and intelligible without further words. The reason for the slowness of the conduction of heat is also easily seen if we look more closely into the process in the way in which Stefan[1] has first examined it.

A heating of one region in a gas consists, according to our theory, in an increase of the molecular speeds in this region. The warmer particles therefore collide with greater momentum against the colder ones near them, and thereby impart a portion of that greater momentum, or, what is the same thing, of their higher temperature, to their environment. In this transference of the energy of motion consists the conduction of heat. This conduction would take place with the speed of the molecular motion if at each collision the striking particle so hit the one struck that the latter moved on in the same direction as that in which the blow occurred. But this happens only on the direct collision of two molecules which were moving in the same or opposite directions; they then simply exchange their velocities, and the whole excess of motion and heat is transferred from the one particle to the other. Mostly, however, the particles collide against each other obliquely; then the particle struck is thrust off in quite a different direction, and it follows that it also receives a much less share of the excess of energy of the other. The transference of heat is therefore not only impeded by its having to follow a zigzag path hither and thither, instead of proceeding in a straight line, but also by only a small fraction of any excess of energy being in general imparted at each collision. It is thus intelligible why a sensible heating cannot spread with the speed of sound in the space occupied by a gas, but only very slowly.

The objections raised are not, therefore, hard to remove. But the raising of them was of great importance for the development of the kinetic theory, and was very beneficial to it. For, owing to that conflict of conceptions, a new and interesting side of our theory has been brought forward which is worth a searching investigation. As in Part I. of this book, the *speed* of the molecular motion and the supply of *energy* therein contained were considered and calculated, so there remain for this Part II. the investigation of the *character* of the motion, the determination of the *length of the path* of a molecule between collisions, and the development of the consequences which will result from our knowledge of these free paths in respect of the different properties and phenomena that have been observed in gases.

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[1] *Pogg. Ann.* 1863, cxix. p. 492; *Wiener Sitzungsber.* xlvii.

## 63. Probability of Molecular Collisions

The pioneer investigation in which Clausius[1] opened out this new wide field cannot, for the attainment of its first aim, viz. the determination of the length of the molecular path, dispense with mathematical expedients. As in Part I., we need again the calculus of probabilities in order to investigate processes which are conditioned by no other law than that of chance. But the demand on mathematical means may be more restricted than it was in the original memoir. It is not necessary to use the higher analysis, and the aid of elementary mathematics is sufficient; the following calculation presupposes no further mathematical knowledge than is needed for the calculation of compound interest.

Before we solve the actual question and determine the probable length of the straight path traversed by a molecule between two collisions, we follow Clausius' procedure in investigating a preparatory and more simple problem. Instead of the actual behaviour of the gaseous molecules, which are all moving about hither and thither, let us imagine the simpler case in which one particle (or a certain number of particles, but all with the same speed and in the same direction) is thrown into a space which is filled irregularly with molecules at rest, their distribution, however, being such that the density is the same everywhere.

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[1] *Pogg. Ann.* 1858, cv. p. 239; *Abhandl. ü. Wärmetheorie*, 2. Abth. 1867, p. 260; *Mech. Wärmetheorie*, iii. 1889–91, p. 55; transl. *Phil. Mag.* [4] xvii. 1859, p. 81.

For the solution of the question bound up with this idea, viz. What path will a particle so thrown in probably traverse without a collision? it is advisable to determine the density of distribution of the particles at rest and express it in terms of their mutual distances apart. If there are $N$ molecules in unit volume, then, considering the volume of this unit to be divided into $N$ equal parts, in fact into $N$ small cubes, we have in each of these small cubes a space which contains on the average only a single molecule. If we denote by the letter $\lambda$ the edge of one of these elemental cubes, which Clausius calls the *mean distance between neighbouring molecules*, the volume of one of the cubes is $\lambda^3$, and the relation

$$N\lambda^3 = 1$$

holds good.

Since the density $\rho$ may be expressed in terms of the molecular weight $m$ and the number $N$ by the formula (§ 13)

$$\rho = Nm,$$

the former formula shows that the density is related to the distance between neighbouring molecules by the equation

$$\rho\lambda^3 = m.$$

From the mean distance $\lambda$ between neighbouring molecules Clausius deduces the *mean probable length of free path* by comparison of that mean distance with the smallest possible distance of separation, *i.e.* with the distance apart of their mean points or centres of gravity at a collision, and of the volume $\lambda^3$ of the elemental cube with the space which the moving particle must at least have for its motion.

If, on the collision of two particles, it happens that they come into actual contact, the least possible distance apart of their centres would be the diameter of either, if we could look upon the molecules as being spheres of equal size; if the molecules have any other shape, the calculus of probabilities allows us to take for this distance the *mean diameter of a molecule.* But it is very conceivable that two molecules cannot come so near each other as to actually touch, but that they are repelled from each other, without actual contact occurring, by forces that come into play at certain, though very small, distances. On account of this possibility it is better that, as already suggested in § 44, we should not put the smallest distance apart of two molecules during a collision as absolutely equal to their diameter. With Clausius, we suppose each molecule to be surrounded by a spherical envelope which is called the *sphere of action,* meaning thereby that the mean point or centre of gravity of another molecule cannot penetrate into it. The radius of this sphere is thus equal to the smallest distance apart of the centres of the particles at the moment of a collision.

By introducing this conception we allow the possibility of the molecules exerting forces upon each other of sufficient strength to prevent actual contact and to cause mutual rebound from each other; we do not, however, thereby, on the other hand, bring in this hypothesis as necessary, as it still remains open to us to assume actual contact on collision; in the latter case we should have to define the sphere of action as eight times the volume of a molecule, and we might call the actual space occupied by a molecule its molecular sphere.

Denoting the radius of the sphere of action by $s$, and, therefore, the area of its central section by $\pi s^2$, we find that if the moving particle considered advances by the mean distance $\lambda$ between neighbouring molecules, its anterior convex surface traverses a cylindrical space bounded by hemispherical ends, the anterior convex and the posterior concave, of volume equal to $\pi s^2 \lambda$. Since there is on the average only a single molecule in a volume equal to $\lambda^3$, the probability that there is a molecule in the cylinder $\pi s^2 \lambda$ described is as much smaller than 1 as $\pi s^2 \lambda$ is less than $\lambda^3$. The probability, therefore, that the particle moved strikes another as it passes over a path of length $\lambda$ is determined by the ratio

$$\pi s^2 \lambda / \lambda^3 = \pi s^2 / \lambda^2,$$

or by the ratio of the central section of the sphere of action to the face of the elemental cube.

On the other hand, the probability that the particle does *not* undergo collision in its path $\lambda$, but passes through a layer of thickness $\lambda$ without colliding with the other particles within it, is

$$1 - \pi s^2/\lambda^2 = (\lambda^2 - \pi s^2)/\lambda^2.$$

We may therefore, to use an ordinary expression, bet $\pi s^2/(\lambda^2 - \pi s^2)$ to 1 that the particle will undergo collision before it passes over a distance $\lambda$, and $(\lambda^2 - \pi s^2)/\pi s^2$ to 1 that it will not collide in this distance.

In these formulæ there lies a simple meaning. If we suppose that the molecule struck were pushed from the interior of the elemental cube containing it into the same face through which the moving particle entered, it would cut out of this face, whose area is $\lambda^2$, a portion equal to $\pi s^2$, through which the entering molecule would not be free to pass; only the remainder $\lambda^2 - \pi s^2$ would allow free entrance for the molecule. The two probabilities therefore have, as indeed they must have, the same ratio as the not-free part to the free part of the face of the elemental cube.

## 64. Probability of a Longer Path being Traversed

From this value of the probability for the traversing of a path of length $\lambda$, or for the passage without collision through a gaseous layer of a thickness $\lambda$ equal to that separating two neighbouring molecules, may be easily calculated the probability for the passage through a thicker layer or for a path of finite magnitude.

For this we suppose $M$ moving particles, instead of one, to be simultaneously projected into the medium, consisting of particles at rest, which we suppose to be divided into a number of layers of thickness $\lambda$. Of these $M$ particles $M\pi s^2/\lambda^2$ will probably undergo collision in the first layer, while only the remainder $M(1 - \pi s^2/\lambda^2)$ will pass through it unhindered. Of these the number that collide in the second layer of the same thickness $\lambda$ is $M(1 - \pi s^2/\lambda^2)\pi s^2/\lambda^2$, while $M(1 - \pi s^2/\lambda^2)^2$ particles pass through this layer. So in the third layer $M(1 - \pi s^2/\lambda^2)^2 \pi s^2/\lambda^2$ collide, and $M(1 - \pi s^2/\lambda^2)^3$ pass through. Proceeding in this manner we see that in the $x$th layer there are probably

$$M(1 - \pi s^2/\lambda^2)^{x-1} \pi s^2/\lambda^2$$

that collide, and thus have traversed a path of length $x\lambda$, while the remainder $M(1 - \pi s^2/\lambda^2)^x$ do not probably suffer collision, and therefore traverse still longer paths.[1]

From this we at once obtain the probability that a single molecule will pass over a given path and then collide, by dividing the probability in the case of $M$ particles by the number $M$, since the probability for one particle must be $M$ times less than for $M$ particles. The probability, therefore, that a moving particle traverses a path $x\lambda$ and collides on its completion is

$$(1 - \pi s^2/\lambda^2)^{x-1} \pi s^2/\lambda^2.$$

## 65. Calculation of the Mean Free Path under Simplified Assumptions

From the foregoing formulæ we can calculate by elementary methods and without great difficulty the probable mean value of the lengths of the paths traversed by all the particles. To find this it is only requisite to calculate the sum of all the different paths traversed by the $M$ molecules and to divide it by their number, that is, by $M$.

Of the $M$ particles there remain $M\pi s^2/\lambda^2$ in the first layer, and these therefore traverse only the path $\lambda$; thus the sum of the paths traversed by these molecules is $M\pi s^2/\lambda$. Similarly, there remain in the second layer, after completing the path $2\lambda$, the number $M(1 - \pi s^2/\lambda^2)\pi s^2/\lambda^2$, the sum of whose paths is therefore $2M(1 - \pi s^2/\lambda^2)\pi s^2/\lambda$. In this way we find in general that the sum of the paths of the particles which collide in the $x$th layer is $xM(1-\pi s^2/\lambda^2)^{x-1}\pi s^2/\lambda$, and the total sum of the paths traversed by the whole of the $M$ particles is therefore

$$\Sigma . xM(1 - \pi s^2/\lambda^2)^{x-1} \pi s^2/\lambda,$$

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[1] This formula is developed in § 26$^k$ in a mathematically simpler form.

where the sign of summation denotes a summation for all integral values of $x$ from 1 to $\infty$. The mean probable length of the free path $L$ of a molecule is therefore given by the formula

$$L = (\pi s^2/\lambda)\Sigma.x(1 - \pi s^2/\lambda^2)^{x-1}.$$

This sum may be easily calculated. For

$$\Sigma.x\phi^{x-1} = 1 + 2\phi + 3\phi^2 + \ldots = (1 - \phi)^{-2},$$

or, in our case,

$$\Sigma.x(1 - \pi s^2/\lambda^2)^{x-1} = (\lambda^2/\pi s^2)^2.$$

Hence it results from this calculation of probability that the *length of the path which a moving particle would traverse without collision amid a multitude of particles at rest* is on the average

$$L = \lambda^3/\pi s^2.$$

This formula, which Clausius deduced in the memoir referred to in a similar way, but with the use of the integral calculus, assumes an intelligible form if we write it

$$L : \lambda = \lambda^2 : \pi s^2;$$

it then expresses that *the mean free path bears the same ratio to the mean distance separating two neighbouring particles as the area of a face of the elemental cube has to the central section of the sphere of action.*

From this proposition Clausius draws a very important conclusion. The above proportion shows indeed that the free path $L$ is greater than the distance of molecular separation $\lambda$, and that it must be very much greater than the latter in a rarefied gas. For by definition $\lambda$ is the edge of the elemental cube in which a single molecule is contained, and $s$, the radius of the sphere of action, is a distance within which the force exerted by the molecule is sensible. It would be in contradiction of our theory, no less than of experiment, which has shown an almost perfect absence of cohesion in gases, if we were not to assume the latter length $s$ to be considerably smaller than the former $\lambda$; consequently also the proportion shows that $L$ is considerably larger than $\lambda$.

*A molecule therefore passes by many molecules like itself before it collides with another.*

## 66. Probability of Particular Free Paths

Now that we have determined the mean value of the molecular free path, the probability-formulæ obtained in § 64 present a simple meaning which makes it possible for us to numerically answer the question, How much more probable is a shorter path than a longer?

The expression $M(1 - \pi s^2/\lambda^2)^x$, which we have found for the probable number of those among the $M$ projected particles that traverse a path greater than $x\lambda$, becomes

$$M(1 - \lambda/L)^x$$

when the mean free path $L$ is introduced into it, so that we can see how the number of the particles which collide in each layer and that of those which pass through it unobstructed depend only on the ratio of the average distance of molecular separation to the mean free path.

If we wish also to refer to the mean free path the actual path traversed, which hitherto has been given by the number $x$, we can put for the path

$$y \equiv x\lambda \equiv qL,$$

where the number $q$ gives the number of times by which the path already traversed by the particle under consideration exceeds the mean free path. If we also put

$$L \equiv Q\lambda,$$

we shall have

$$x = Qq,$$

and the probable number of particles which do not undergo collision in a path of length $qL$ is given by

$$M(1 - 1/Q)^{Qq}.$$

We do not indeed know the number $Q$, *i.e.* the ratio of the mean free path to the distance of molecular separation, which occurs in this expression, but we do know that its value must be very great, so great indeed that we may look upon it as almost infinitely great. If $Q$ were actually infinitely great, we should have

$$(1 - Q^{-1})^{Q} = e^{-1} = 1/2{\cdot}718\ldots = 0{\cdot}36788,$$

where $e$ is the base of natural logarithms.

Therefore the number of particles which traverse a path at least $q$ times greater than that passed over in the mean is, with this assumption,

$$M(1 - Q^{-1})^{Qq} = Me^{-q}.$$

According to this formula we have calculated the following table. Out of every 100 particles

| | | | | |
|---|---|---|---|---|
| 99 | traverse | the | path | 0·01 $L$ |
| 98 | ,, | ,, | ,, | 0·02 $L$ |
| 90 | ,, | ,, | ,, | 0·1 $L$ |
| 82 | ,, | ,, | ,, | 0·2 $L$ |
| 78 | ,, | ,, | ,, | 0·25 $L$ |
| 72 | ,, | ,, | ,, | 0·333 $L$ |
| 61 | ,, | ,, | ,, | 0·5 $L$ |
| 37 | ,, | ,, | ,, | 1 $L$ |
| 14 | ,, | ,, | ,, | 2 $L$ |
| 5 | ,, | ,, | ,, | 3 $L$ |
| 2 | ,, | ,, | ,, | 4 $L$ |
| 1 | ,, | ,, | ,, | 4·6 $L$ |

without collision.

The table shows that the mean free path is considerably exceeded extremely seldom. The only play of chance, therefore, is to set up in this case too, as well as in that of the distribution of speeds, a uniformity that is maintained with great exactness.

## 67. Free Path if all the Molecules have Equal Speed

The value we have found for the mean free path needs still a correction, which the considerations of the last paragraph do not, however, touch.

The value of the mean free path found in § 65, viz.

$$L = \lambda^3/\pi s^2,$$

holds only for a simple hypothetical case described fully in § 63; it was supposed that only the one particle whose free path we were calculating was in motion, all the others being at rest. All the particles, however, are in motion in the actual case. It is easy to see that this general motion must increase the probability of a collision of one particle with the others; for the particle can also be struck by another that moves from the side and with which it would not come into contact as a result of its own motion. By the general motion, therefore, of all the particles the probability of a collision is increased, and thus the mean value of the molecular free path is diminished.

Clausius has calculated this shortening of the path for the case in which all the particles move with equal speeds but in all possible directions in space. With this supposition we find the number of collisions increased in the ratio of 4 : 3, and, therefore, the free path shortened in the ratio 3 : 4. We obtain then, as is proved in § 28*, the value

$$L = \tfrac{3}{4}\lambda^3 / \pi s^2$$

for *the mean free path of a particle in the uniformly moving medium*, and this differs only by the factor $\frac{3}{4}$ from the former value. From this equation also we can deduce a proportion like the former and of similarly simple meaning, viz.

$$L : s = \lambda^3 : \tfrac{4}{3}\pi s^3.$$

## 68. Molecular Free Path with an Unequal Distribution of Speeds

But these calculations do not correspond exactly to the real state of things, since the underlying assumption as to the way in which the speeds are distributed among the molecules cannot possibly be right. The supposition that all the particles of a gaseous medium are to have equal speeds gives no real picture of the motion which exists in a gas that is in equilibrium under a pressure which is everywhere the same and at a temperature which is everywhere the same. The true law according to which the molecules arrange their speeds is, as we know (§ 24), that discovered by Maxwell.

Maxwell[1] has also calculated the mean value of the free path on the assumption of this law. The calculation cannot be here given; a deduction of the formula will be found[2] in § 29*.

The result of the calculation agrees almost exactly with that just mentioned which Clausius obtained on the assumption of equal speeds in the molecules. In this case, too, the formula demonstrated in § 65 undergoes no further alteration than the addition of a numerical factor, and there results for the mean free path

$$L = \lambda^3 / \pi s^2 \sqrt{2}.$$

The factor, the value of which will be more closely indicated in § 96, is nearly the same as that in Clausius' formula; for the latter is $\frac{3}{4}$ or 0·75, and the former $1/\sqrt{2}$ or 0·707, so that they are approximately in the ratio of 17 to 16 [or, still more nearly, of 35 to 33].

The value of the free path that follows from Maxwell's law is somewhat the smaller; there also results from this law a smaller value of the mean speed than that given by Clausius' theory; both results are explained on the simple ground that a shorter path and a slower speed occur more frequently than a longer path and a higher speed.

## 69. Molecular Path-volume

The name of molecular path-volume has been given by Loschmidt[3] to the content of the cylindrical space which a molecule describes when it traverses its mean free path. The magnitude of this volume is $\frac{1}{4}\pi s^2 L$, since the radius of the sphere of action is equal to the distance apart of the middle points of two molecules during collision, and is, therefore, equal to the diameter of a molecule in the case of actual contact during collision; hence by the foregoing formula it is equal to $\lambda^3/4\sqrt{2}$. If we replace in this expression the size of the elemental cube, or of the space that contains a single molecule only, by the number $N$ of molecules contained in unit volume which is given by $N\lambda^3 = 1$, we find that the molecular path-volume is determined by the expressions

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[1] *Phil. Mag.* 1860 [4] xix. p. 28; *Scientific Papers*, 1895, i. p. 387.

[2] Compare § 97.

[3] *Wiener Sitzungsber.* 1865, lii. Abth. 2, p. 397.

$$\tfrac{1}{4}\pi s^2 L = \lambda^3/4\sqrt{2} = 1/4\sqrt{2}N,$$

which show that its value is the same for all gases, since, according to Avogadro's law, the number $N$ has the same value for all kinds of gas.

## 70. Frequency of Collisions

From the value of the free path and of the known magnitude of the molecular speed we can without difficulty determine the frequency of the collision of any particle with others, and the time which on an average elapses between two successive collisions. We need only remember that the speed is simply measured by the length of path traversed in the unit of time.

If now a particle traverses on an average in unit time the path $\Omega$, which in general is zigzag-shaped, and between two successive collisions passes over the average length $L$ in a straight line, the time required on an average for the particle to move over the length $L$ is

$$T = L/\Omega.$$

From this *interval between successive collisions* we obtain the *frequency of collision* or the number of collisions that a particle undergoes in unit time, viz.

$$1/T = \Omega/L.$$

If we put for the speed in these formulæ the arithmetic mean $\Omega$ calculated by Maxwell's theory, we must also put for the free path $L$ the value

$$L = \lambda^3/\pi s^2\sqrt{2},$$

as calculated (§ 68) on the same theory.

If, on the contrary, in accordance with Clausius' theory, we assign to all the molecules the same mean energy and the same value $G$ of the speed which corresponds to it, the interval between successive collisions in this case would be

$$T' = L'/G,$$

where $L'$ is the value of the free path as deduced in § 67 on this assumption, viz.

$$L' = \tfrac{3}{4}\lambda^3/\pi s^2,$$

and where

$$G = \Omega\sqrt{(3\pi/8)}$$

as in § 27. Thus between these two values there is the ratio

$$T' : T = \sqrt{3} : \sqrt{\pi}$$

[or very nearly as 43 : 44]; the interval between successive collisions is thus somewhat smaller, and the collision-frequency a little larger on Clausius' theory than on Maxwell's.

## 71. Relations of the Free Path to the Pressure and Temperature

According to the theoretical formula we have found, the value of the molecular free path depends only on the volume $\lambda^3$ of the elemental cube and the area $\pi s^2$ of the central section of the molecular sphere of action; the molecular speed $\Omega$, by which the value of the temperature of the gas is determined, does not, however, occur in the formula.

Of these two magnitudes the elemental cube denotes the small volume in which, on the average, each single molecule only is contained. The size of this space is not altered by mere addition of heat, but can only be altered by the volume of the gas becoming greater or less; it is proportional to this volume, and therefore varies inversely as the density, but is independent of the temperature of the gas.

If now the size of the sphere of action were not variable with either the pressure or the temperature of the gas, it would follow that the molecular free path cannot depend on the temperature, but only on the density of the gas; and, indeed, must decrease or increase inversely proportionally to the density, and therefore, if the temperature remains constant, inversely proportionally to the pressure, by reason of Boyle's law.

The assumption that the sphere of action of a molecule is actually altered neither by pressure nor by heat has much to entice us; for we have become used to consider a molecule as an aggregate of atoms which can certainly be altered by chemical transformations, but not by processes which belong to the narrower region of physics. If this doctrine, which in former days ruled without question, were true, the size of the molecular sphere of action could not be conditioned by the temperature or the pressure of the gas.

But this view is contested by abundant observations and especially by the phenomena of dissociation. Numerous instances of gases and vapours can be cited wherein the molecules are composed of more atoms at lower temperatures than at higher. The vapours and many gases deviate at low temperatures from the laws of the ideal state of gas, especially from those of Boyle and Gay-Lussac, as has been already described in Chapter IV., these deviations being such that the gases have too great a density and an expansibility which is much greater than that of ideal gases. These and many other irregularities force us to the conclusion that the molecules of those gases form bigger aggregates of molecules at lower temperatures than at higher. By increment of heat the molecules break up into smaller ones, and therefore the mass of the molecule is decreased by rise of temperature; consequently their extension in space, and therewith the size of their sphere of action, will both become smaller when the temperature rises. From this we should expect that, by reason of dissociation, the molecular free path for vapours and non-perfect gases increases as the temperature rises.

Moreover, even for gases which undergo no dissociation of their molecules, it is possible to suppose that a diminution of the molecular sphere of action may occur and demand explanation. We have only to remember that the sphere of action need not denote the space which the molecule itself occupies or claims for itself; but its radius is the least distance to which the centres, or, more generally, the centres of gravity, of two molecules can approach each other during a collision. To assume that this distance is smaller at higher temperatures than at lower entails nothing that is at all contrary to either reason or probability. For the speed of the particles increases with the temperature, and, therefore, also the intensity of the stress during collision, and it is easily conceivable that the more strongly the particles collide, the nearer they approach each other.

We might perhaps suppose that the molecules become looser in their joints during rise of temperature—this is a safe assumption at least with compounds—so that one penetrates into another the more easily and deeply the warmer they are.[1] Or we might assume with Stefan[2] that the molecules are surrounded by atmospheres of ether which, like elastic bodies, are compressed the more during a collision the more intense the blow. We could, finally, share Maxwell's[3] view, according to which two molecules that collide are repelled from each other because, when they approach very near together, they act on each other with repulsive forces. On all these different hypotheses the particles must come the nearer together the greater their relative velocity; or, in other words, the sphere of action is the smaller the higher the temperature, and we ought therefore to expect that the molecular free path increases with rising temperature. This has in fact been proved, as will be later shown, by measurements on viscosity and allied phenomena.

W. Sutherland[4] has attempted to give an essentially different explanation of these facts. He assumes forces between the gaseous particles, when very near together, which are not repulsive, as Maxwell takes them, but, on the contrary, attractive; his supposition agrees, therefore, the best with the known observations which Joule and Lord Kelvin[5] made on the heat-phenomena of certain gases streaming from a holder. These attractive forces do not remain without effect on the molecular free path; for by such forces as cause approach the probability of a collision is increased, and the mean probable value of the molecular free path is therefore diminished.

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[1] *Pogg. Ann.* 1873, cxlviii. p. 233.

[2] *Wiener Sitzungsber.* 1872, lxv. Abth. 2, p. 339.

[3] *Phil. Trans.* 1866, clvi. p. 257; 1867, clvii. p. 51. *Phil. Mag.* 1868 [4] xxxv. p. 133. *Scientific Papers*, ii. pp. 11, 29.

[4] *Phil. Mag.* 1893 [5] xxxvi. p. 507.

[5] *Phil. Trans.* 1853, cxliii. p. 357; 1854, cxliv. p. 321; 1860, cl. p. 325; 1862, clii. p. 579.

The process by which Sutherland calculates the amount of diminution of the free path is given in § 35*; I prefer here another way of attaining this object without much calculation.

Whether the attractions will bring about an encounter of two particles that pass close by each other, or not, depends on the amount of the two kinds of energy, one of which furthers the encounter, while the other hinders it. While the kinetic energy which the particles possess by reason of their speed, as they rush close by each other, opposes a deviation from the rectilinear path, and, therefore, also the probability of an encounter, the potential energy of the attractive forces, on the contrary, has the effect of promoting the encounter. The number of collisions will therefore be the more increased by the molecular energy the greater the amount $E$ of potential energy which comes into activity on the approach of one particle from an infinite distance to entrance into the sphere of action of another; but this increase will be so much the smaller the greater the kinetic energy of the particles. Hence we assume that the number of encounters which a particle undergoes in unit time, by reason of the attractive forces, is increased by a magnitude which is proportional to the given potential energy $E$, and, on the contrary, is inversely proportional to the mean kinetic energy of the gaseous molecules, and thus inversely proportional to the magnitude

$$\tfrac{1}{2}mG^2,$$

in which $m$ is the molecular weight of the gas and $G$ represents Clausius' mean value of the molecular speed (§ 27).

According to a formula of § 70, the number of encounters in unit time without reference to the molecular attraction is

$$1/T = \Omega/L = \sqrt{2}\pi s^2\Omega/\lambda^3;$$

this is increased in consequence of the attractive forces, and, in accordance with the hypothesis just mentioned, may be put as

$$1/T = (1 + 2kE/mG^2)\sqrt{2}\pi s^2\Omega/\lambda^3$$

$$= \frac{\frac{1}{2}mG^2 + kE}{\frac{1}{2}mG^2}\sqrt{2}\pi s^2\Omega/\lambda^3$$

where $k$ denotes a numerical factor. But now $\frac{1}{2}mG^2 + E$ is the total amount of energy of a gaseous particle; if then we were to put $k = 1$, the formula

$$1/T = \frac{\frac{1}{2}mG^2 + E}{\frac{1}{2}mG^2}\sqrt{2}\pi s^2\Omega/\lambda^3$$

would indicate that, owing to forces of cohesion, the number of encounters is increased in the ratio in which the whole energy stands to the kinetic energy. But this would be an assumption which, by its very simplicity, may convince us of its truth, and there is scarcely any need of the mathematical proof of it contained in Sutherland's calculation, which is given in § 35*.

For the application of the theory to the calculation of observations we do not need the assumption $k = 1$, since we can express the result of our considerations even more simply without it. Considering that, according to §§ 14 and 15, the magnitude $G^2$ is proportional to the absolute temperature $\Theta$, while $k$, $m$, and $E$ do not depend upon it, we see that the ratio in which the collision-frequency is increased by the cohesion, viz.

$$1 + 2kE/mG^2 : 1,$$

may also be brought into the form

$$1 + C/\Theta : 1,$$

where $C$ denotes a constant depending on the nature of the gas but not on its temperature.

Hence the collision-frequency appears as a magnitude

$$(1 + C/\Theta)\sqrt{2}\pi s^2\Omega/\lambda^3$$

which depends in a twofold manner on the temperature;

for while the factor $\Omega$ increases with $\Theta$, the newly added factor diminishes as $\Theta$ increases.

The value $L$ of the molecular free path is altered for the same reason in inverse ratio to the collision-frequency. It must be represented by the improved formula

$$L = L_0(1 + Ca)/(1 + C/\Theta),$$

in which $L_0$ denotes the value that holds at the temperature of melting ice, and therefore at $\Theta_0 \equiv 1/a = 272{\cdot}5$ degrees above absolute zero, $a$ being the coefficient of expansion of the gas. According to this formula, the free path $L$ increases with the temperature $\Theta$.

The extent of increase to be expected from this theory may be easily judged by considering the two possible limiting cases. If there were no cohesion, there would be no increase of $L$ with the temperature; if the cohesion is so great that the numerical value of $\Theta$ is small in regard to $C$, the factor

$$1/(1 + C/\Theta) \equiv \Theta/(C + \Theta)$$

approximates to proportionality with $\Theta$, and the more so the greater $C$. The free path therefore increases with rise of temperature at most as greatly as the temperature estimated from absolute zero, and consequently in a slighter ratio in general. (Compare § 87.)

## 72. On the Absolute Value of the Free Path

The absolute magnitude of the number of collisions of a molecule that occur in unit time—a second, for instance—can be determined from the above formulæ just as little as the value of the mean free path in absolute measure—millimetres, for instance. For the latter depends on two unknown magnitudes, viz. the mean distance of molecular separation $\lambda$ and the radius of the sphere of action $s$. With respect to these we only know, as has already been mentioned in § 65, that $\lambda$ must be very much larger than $s$, and therefore $L$ very much larger than $\lambda$.

Although, therefore, a molecule passes by many molecules like it, perhaps many thousands, without obstruction, before it finally collides with another, yet the absolute value of the free path, as measured in our usual units, may be an insignificantly small magnitude on account of the extreme minuteness of the distance of molecular separation.

It is on these circumstances that the possibility of explaining the apparent contradiction between the phenomena mentioned at the beginning of Part II. (§ 61) and the theory developed in Part I. depends. The fundamental hypothesis of the latter—of molecules rapidly moving in straight paths—does not exclude the other, viz. that the lengths of these paths, measured in ordinary units, are very small; it is sufficient that they should be large in comparison with the dimensions and the distances apart of the molecules for the justness of Clausius' assumption to be upheld; for then it is allowable to suppose that the length of path which a molecule passes over in a straight line between successive collisions may be considered as infinitely great in comparison with the curved path it traverses while casually within the sphere of action of another.

Whether this mode of getting over the difficulty is right and based on actuality is for observation to decide. We turn, therefore, to the experimental methods of actually measuring molecular free paths, and to this end we proceed to the consideration of the viscosity, diffusion, and heat-conduction in gases.

# CHAPTER VII

## *VISCOSITY OF GASES*

### 73. On the Character of Internal and External Friction

By the name of *internal friction*[1] Newton has denoted a property of fluid media which is also termed *viscosity*. This property exhibits itself in phenomena whose cause we might be inclined to look for in a cohesion which is exerted during motion and acts in opposition to motion, and perhaps we should not be wrong in the case of liquids; in gases, however, which have no sensible cohesion, we must look for another cause, and perhaps therefore in liquids too.

To push a solid body on a liquid at rest, or one liquid layer over another, a certain force is required, just as force must necessarily be employed when a solid body is rolled or slidden along a solid support at rest. Analogy justifies the use of the word *friction* to all these phenomena, and therefore the ascription of friction to fluid media and not alone to solids. So by the *external friction* of a fluid we mean the friction that is brought into play at the surface of separation of the fluid and a solid body or of two fluids, while as *internal friction* we denote that friction which acts between layers of one and the same fluid which move with different speeds.

It is not difficult to see the reason why force must be employed to overcome this, which is perhaps only apparently friction in the fluid. When a body is moved either in or upon a fluid it puts the fluid also into motion, and thus loses a part of its energy, just as by friction against a solid support;

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[1] 'Attritus vel resistentia quæ oritur ex defectu lubricitatis,' *Philosophiæ Naturalis Principia Mathematica*, 1687, lib. ii. sect. 9.

and if this loss is to be replaced force must be employed. Just in the same way, a fluid which streams along the surface of a movable solid or of a second fluid loses part of its speed by imparting motion to that other solid or fluid body.

What was said about external friction in these cases applies also to the internal friction of fluids. If inside a fluid one layer moves more quickly than its neighbours, it drags them along with it, and loses a part of its speed by giving it up to them, just as a moving body loses speed by friction with its support.

The friction of fluids, therefore, both internal and external, consists only in a transfer of motion; but this transfer does not proceed without loss: a part of the translatory motion of the layers is transformed into heat, and, since this change into heat is continually going on, the motion of translation is in time all changed into heat-motions, and mechanical motion is annihilated as in the case of friction between hard bodies. This change into heat becomes complete at once if the body on whose surface the friction is exerted is fixed and immovable.

This transformation into heat, also, is easy to understand. Heat-motion differs from translatory motion only in the particles moving in all possible directions, without distinction, and not, as in the latter case, all in one and the same direction. Change, therefore, of mechanical motion into heat-motion consists in nothing else than a change of the direction in which individual particles move. A multiform change of direction of this kind cannot fail to occur in the crowd of particles of which the medium consists if these particles exert actions upon each other either by forces of cohesion or by collisions; and therefore, along with the transfer of speed, which is called friction, there must also occur a partial transformation into heat.

## 74. Newton's Fundamental Law of Internal Friction

The force which causes the transfer of motion from one layer to another when internal friction occurs in a fluid has already been recognised by Newton as a kind of pressure which acts on the limiting faces of the two layers. But by this we must not think of a pressure in the hydrostatic sense, which acts equally in all directions, and whose action on a surface is always directed normally to that surface; just as the elastic forces in a body depend as to their magnitude and direction upon its changes of shape, and therefore on the shifting of its particles, so must the frictional pressure depend as to its magnitude and direction on the magnitude and direction of the motions that take place. Its value, therefore, may be different according to the position of the surface of pressure or friction in respect of the direction of the motion.

The way in which the magnitude of this pressure depends on the velocity that is present cannot be completely determined by theoretical considerations. There is nothing else, therefore, for us but to make up for our defective knowledge by a hypothesis, and afterwards to make trial of its soundness by comparing the conclusions drawn from it with the results of experiment.

Only one hypothesis has been recognised as certain, viz. that the amount of the friction exerted between two layers can depend only on their *relative* motion, and therefore only on the difference between their velocities; for if both layers move with the same speed in the same direction, neither gives to the other, and no friction occurs. Starting from this consideration, Newton has put forward the hypothesis that *the internal friction is directly proportional to the difference in velocity of neighbouring layers*, so that, for instance, a doubling of the friction results from a doubling of both velocities.

The internal friction must further depend on the nature of the medium, so that a more viscous fluid experiences a greater friction and a thinner fluid a less friction. Such a dependence on the matter may be expressed by a numerical factor by which the mathematical expression of the frictional pressure is multiplied. This numerical factor which gives a numerical measure of the viscosity or the friction of the fluid is called the *coefficient of friction* or *of viscosity*.

The following illustration gives an insight into the meaning of this coefficient of viscosity. Let a fluid, whose depth is equal to the unit of length, move over a horizontal plane, and let its motion have become stationary and be of such character that all the particles in the same horizontal plane have the same velocity. A necessary consequence of this is that the velocity is given by a linear function of the height above the base. For in this state of motion each layer experiences on its two sides equal and oppositely directed friction, so that no change can occur in the velocity of a layer. If we further assume that the lowest layer sticks fast to the base, and that, on the contrary, the highest layer has such a velocity that it moves over unit length in unit time, so that the speed in each layer is numerically equal to the height, then the friction on unit area which is exerted between any two neighbouring layers of this fluid is equal to its coefficient of viscosity.

The measurement of the internal friction of a medium consists in the determination of the value of this coefficient; it is a constant magnitude if Newton's assumption—that the friction is proportional to the relative velocity—is really true. Newton's theory will therefore be proved to be true if different measures of the internal friction, especially if made by different methods, give the same value for this constant.

Such an agreement of measures has really been found, both for liquids and for gases, as will be described later in fuller detail. In gases a perfect agreement with experiment has also been found for those properties which, on the kinetic theory of gases, are connected with the coefficient of viscosity.

## 75. Formula for the Coefficient of Viscosity of a Gas

To establish the properties of the viscosity-coefficient of a gas on our theory it suffices to carry out in greater particularity, in the sense of our theory, the analysis of the process, called internal friction,[1] which has already been given in general terms.

If, according to that analysis, the internal friction consists in a transfer of the motion of flow from one layer to another, and in a transformation of the motion so transferred into heat-motion, then *no gas can be free from internal friction.* For the molecules carry over velocity from one place to another by their very hither-and-thither motions, and by their frequent encounters the directions of their motions undergo continual change, so that the flow of the gas which existed at the beginning, and in which all the molecules moved in the same direction, must gradually be changed into a motion that proceeds in all possible directions, that is, into heat. The phenomenon of internal friction is therefore explained by the kinetic theory in an unforced manner.

Our theory, however, gives more than this explanation on general lines; since the friction is caused by the exceedingly rapid motion of the molecules, the theory justifies us in concluding, in agreement with experiment, that *gases possess no little viscosity,* and that *this viscosity will increase with the temperature,* since the speed increases with the temperature.

We obtain the amount of the friction brought into play by summing the momentum which is carried over from one layer into another by reason of the heat-motion of the molecules, for on our explanation this momentum and the friction are identical. To form directly the measure of the viscosity given above, *i.e.* the coefficient of viscosity, I start for the calculation of this sum from the illustration given in § 74, wherein a gas flows over a horizontal surface in the immediate neighbourhood of which it is at rest, elsewhere flowing parallel to the surface, and so that the velocity is the same at all points of a horizontal plane; we further take the velocity of flow at a distance $x$ above the base to be numerically equal to $x$, that is,

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[1] Maxwell, *Phil. Mag.* 1860 [4] xix. p. 31. O. E. Meyer, *Pogg. Ann.* 1865, cxxv. p. 586. Maxwell, *Phil. Mag.* 1868 [4] xxxv. p. 209. V. von Lang, *Wiener Sitzungsber.* 1871, lxiv. Abth. 2, p. 485; *Pogg. Ann.* 1871, cxlv. p. 290; *Einleitung in die theor. Physik.* 1867, p. 526. Stefan, *Wiener Sitzungsber.* 1872, lxv. Abth. 2, p. 360. Boltzmann, *ibid.* 1872, lxvi. Abth. 2, p. 324; 1880, lxxxi. Abth. 2, p. 117; 1881, lxxxiv. Abth. 2, pp. 40, 1230; 1887, xcvi. Abth. 2, p. 891.

$$v = x,$$

or we assume that each particle passes in unit time over a distance which is equal to its height above the base. In this distribution of flow the friction per unit area between any two layers is equal to the coefficient of viscosity.

Besides this forward velocity $v$ there is the heat-motion of the gas. In comparison with this exceedingly rapid motion, which in air, for instance, has at 0° a mean speed of 447 metres per second, the assumed forward velocity $v$, which at the height $x = 1$ metre is only 1 metre per second, is vanishingly small. The addition of this new motion will therefore exert no sensible effect on that heat-motion or on the length of free path, the collision-frequency, &c., so that we can reckon the number of particles which leave one layer and pass over into another as if they had their molecular speed only.

We calculate the friction between two layers which lie the one on the other, with the horizontal plane at the height $x$ above the base for their plane of contact, by exactly the same method as we used in § 12 to calculate the pressure in the interior of a gaseous mass. We put the number of particles, which in unit time pass through unit area of the limiting plane from the lower layer to the upper, equal to $\frac{1}{6}NG$; for this we assume, as was first suggested by Joule, that only a third of the $N$ particles in unit volume come into account as regards passage in a given direction, and, as before, we take $G$ to represent the mean value of the speed as deduced from the mean kinetic energy (§ 27).

The particles forming this number have begun their path towards the limiting layer at different depths, but on the average they come from a distance from this layer which is equal to the mean free path $L$, and therefore from a layer which is at the height $x - L$ above the base. Their mean forward velocity is therefore given by

$$v' = x - L,$$

and the momentum which is carried over on the average by every single molecule from the lower to the upper layer amounts to

$$mv' = m(x - L)\,;$$

on the whole, then, the momentum

$$\tfrac{1}{6}NmG(x - L)$$

is carried in unit time over unit area of the plane at the height $x$ by the particles which cross the plane from the layers below it to those above.

There simultaneously goes in the opposite direction from the upper to the lower layers the amount of momentum

$$\tfrac{1}{6}NmG(x + L).$$

Therefore the layers above the limiting plane lose in unit time the momentum

$$\tfrac{1}{6}NmG(x + L) - \tfrac{1}{6}NmG(x - L) = \tfrac{1}{3}NmGL,$$

while the lower layers gain the same amount. According to the explanation of viscosity, which we have given in the sense of the kinetic theory, the internal friction exerted on unit surface is therefore

$$\eta = \tfrac{1}{3}NmGL,$$

and this magnitude is the coefficient of viscosity of the gas.

The formula we have obtained has an unmistakable likeness to that found for the pressure, viz.

$$p = \tfrac{1}{3}NmG^2\,;$$

it differs from it only by having the free path $L$, *i.e.* a magnitude of the dimensions of length, in place of the factor $G$ which denotes the molecular velocity. Thus the idea of friction being a kind of pressure, which was brought forward in § 74, is justified, and the value of a coefficient of viscosity may be referred in the same way[1] as a pressure to the usual units, the gram, centimetre, and second.

To avoid, however, all uncertainty afterwards, we must point out that it would be incorrect to leave out of account the difference between the two magnitudes, a velocity and a free path; for a velocity is not, like a path, measured only by a length, but for its complete specification it requires a time unit also to be laid down. It is therefore well not to express the numerical values of the friction in the way usual for values of pressure, but, after deduction of the formula, which on replacement of $Nm$ by the density $\rho$ we bring into the form

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[1] [The dimensions are, however, not the same; those of $p$ are $ML^{-1}T^{-2}$, and those of $\eta$ are $ML^{-1}T^{-1}$.—Tr.]

$$\eta = \tfrac{1}{3}\rho G L,$$

to refer them to the units of density, length, and time. We thereby obtain also this advantage, that the numerical values become independent of the value of gravity, which alters with the latitude of the place of observation. I shall therefore give the numerical values of the viscosity which follow in such units that they contain the density of water, the centimetre or square centimetre, and the second as fundamental units.

## 76. Theoretical Laws of Gaseous Friction

The final formula of the kinetic theory of viscosity, which was found by Maxwell,[1] leads to a very surprising result if we introduce into it the value of the free path.

Since we have worked out the above considerations as if all the molecules possessed equal speeds and attained equal free paths—a mode of calculation which is sufficient only for an approximation—we must use the Clausius expression for the free path, and not that of Maxwell. Referring to the Mathematical Appendix (§§ 46*–48*) for the stricter calculation of viscosity, we put here

$$L = \tfrac{3}{4}\lambda^3/\pi s^2$$

with Clausius, and find for the viscosity-coefficient the value

$$\eta = N\lambda^3 m G/4\pi s^2.$$

In this formula $N$ is the number of molecules per unit volume, and $\lambda^3$ the volume occupied by a single molecule; consequently $N\lambda^3 = 1$, as we have already (§ 63) several times seen, so that the coefficient of viscosity takes the simpler form

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[1] *Phil. Mag.* 1860 [4] xix. p. 31; *Scientific Papers*, 1890, i. p. 390.

$$\eta = mG/4\pi s^2.$$

In this form the expression for the viscosity-coefficient contains no factor which at all depends on the pressure of the gas, but only magnitudes which depend on the mass, speed, and sphere of action of the molecules, and thus generally on their state. The formula therefore gives the proof of the well-known law of Maxwell that *the viscosity of a gas is independent of its density.*

At first sight this law must seem but little probable. According to it the friction should retain the same intensity when the gas increases in rarity. This seems to lead to a conclusion which, although apparently admissible by the last formula, contains a contradiction in itself, viz. that a gas rarefied to density 0, and thus rarefied out of existence, exerts the same friction as one that actually exists. We see the fallacy of this conclusion[1] when we consider how the formula was obtained; it is a transformation of the formula

$$\eta = \tfrac{1}{3}\rho L G$$

given in § 75, according to which the viscosity $\eta$ vanishes with the density $\rho$, so long as neither the mean free path $L$ nor the mean speed $G$ becomes infinitely great. But this limiting case is obviously excluded in the deduction of the formula given in § 75, and therefore the theoretical formula no longer holds for the coefficient of friction in the limiting case for which $\rho = 0$.

With the exception of this limiting case, Maxwell's theoretically deduced formula seems still surprising enough to justify our more closely describing the causes of its being obtained which are hidden in the mathematical reasoning. For such an explanation in words the last formula, whose meaning is easily perceived, offers itself suitably. The friction $\eta$ is the quantity of momentum which is carried over from layer to layer under the before-mentioned circumstances. The transfer occurs by means of the heat-motions of the molecules; consequently, as the formula shows, it must be proportional to the speed $G$. It, further, is carried out by the molecules themselves, and therefore will be the greater the more there are of them; hence the formula for the friction contains the density of the gas as a second factor. The transfer can only take place between layers whose distance apart can be traversed by a molecule; the friction must therefore be the greater the wider the range of effective layers, and it must therefore, in the third place, be proportional to the molecular free path. The fourth factor, the coefficient $\frac{1}{3}$, is explained in the same way as in the exactly similar formula for the pressure, namely, by the circumstance that only a third part of the molecules which are moving in all directions, and therefore symmetrically with respect to the three dimensions of space, come into account in regard to transference in the direction of one of these three dimensions.

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[1] Compare further § 81.

This explanation of the formula we have found contains at the same time a reason for this remarkable law. Of the factors in the formula there are only two, $\rho$ and $L$, which are variable with the compression or rarefaction of the gas, and they vary so that, if the density $\rho$ increases, the free path $L$ of the molecules, which are hindered in their motion by the constriction of the space containing them, becomes smaller and *vice versa.* In this way it is possible that the product of these two quantities, of which one increases while the other diminishes, may always keep the same value; and therefore after this consideration the paradoxical law of Maxwell will have lost much of its improbability.

The coefficient of viscosity is not, however, independent of the temperature, as it is of the pressure. Of its factors only $G$ and $L$ can be variable with the temperature. With respect to the former we know from experiments on the pressure of gases that it is proportional to the square root of the absolute temperature, or that it increases with the temperature $\vartheta$ measured on the usual scale in the ratio $\sqrt{(1 + a\vartheta)} : 1$, where $a$ denotes the thermal coefficient of expansion of the gas. As to the free path $L$, the theory leaves it undecided whether it alters with the temperature or not. The simplest assumption would be that it does not depend upon temperature; but, as we have seen in § 71, other possibilities are not excluded. From this, then, we cannot take it as certain, but only as a probable consequence of the theory, that the viscosity of gases increases with the temperature. Gases would therefore in this respect behave oppositely to liquids, whose viscosity is the less at the higher temperatures.

## 77. Observations on the Friction of Gases at Different Pressures

The remarkable laws of the viscosity of gases deduced by Maxwell in 1860 from the kinetic theory of these media challenge experimental proof, not only on account of their apparently innate improbability, but also especially because an experimental proof of the laws of viscosity might in general give at the same time a decision as to the truth and admissibility of the kinetic theory. For if we do not verify by experiment the laws that are consequences of the theory, the theory which requires them must be rejected as erroneous. The importance of this question prompted both Maxwell and myself almost simultaneously to carry out experimental investigations, which were published in the next following years, and were founded on exactly similar methods.

Of the methods employed up to that time for the determination of the viscosity of liquids, that invented by Coulomb[1] presented itself first of all as the most suitable, because with it the same pressure is exerted everywhere throughout the gas investigated. If a circular disc is suspended horizontally by a wire fastened to its centre, it may, by means of the torsion of the wire, be put into oscillation in its own plane about that centre. If the disc is in a fluid, the amplitude of the oscillations will gradually decrease by reason of the friction which is exerted on each other by the layers of the fluid that are set in motion, and, indeed, the decrease of successive amplitudes follows the law of a geometrical progression. If we measure the amount of decrease, and determine therefore the so-called logarithmic decrement of that progression, we can from the observed magnitudes calculate the amount of friction that has taken place and the value of the coefficient of viscosity. The external friction that also comes into play in the experiment, that is, the friction that occurs between the fluid and the surface of the disc, may be eliminated by repetition of the experiments with more discs of various sizes.

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[1] *Mém de l'Inst. National*, an IX, iii. p. 246.

To make this method more suitable for the determination of the friction of the air, I altered it in my own experiments[1] by employing three oscillating discs with a common axis, instead of one, and arranging them either apart from each other so as to put into oscillation by their six faces the air above and below each of them, or all close together, like a single disc, so as to move the air by two faces only. The combination of the results of the two experiments allowed the coefficient of viscosity to be calculated in a simple way from the difference of the two observed logarithmic decrements. Determinations of the coefficient of viscosity of air carried out at different pressures by this method did not, indeed, show a *complete* agreement with each other as Maxwell's theory required, but the differences between the values found were small enough to prove the law at least within certain limits of the pressure. As an instance I cite the numbers[2] which I obtained by experimenting with an apparatus provided with three glass discs. Since the method does not lead directly to a knowledge of the viscosity-coefficient itself, but rather, first of all, to the square root of the coefficient, I put the latter, referred to centimetres, in the following table, which contains also the temperature and the pressure, the former in Centigrade degrees, the latter in centimetres of mercury.

| $\vartheta$ | $p$ | $\sqrt{\eta}$ | $\eta$ |
|---|---|---|---|
| 17·6 | 74·91 | 0·0136 | 0·000185 |
| 19·6 | 49·97 | 148 | 218 |
| 20·1 | 25·05 | 127 | 162 |
| 21·6 | 1·18 | 110 | 122 |

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[1] *Amtl. Ber. der Naturf.-Vers. in Stettin*, 1863, p. 141; *Pogg. Ann.* 1865, cxxv. p. 177.

[2] Calculated on an improved theory (*Sitzungsber. d. Münchener Akad.* 1887, xvii. p. 343; *Wied. Ann.* 1887, xxxii. p. 642), account being taken of a correction suggested by W. König (*ibid.* 1887, xxxii. p. 193).

I could, however, deduce in all strictness the proof that the viscosity of gases is really independent of the pressure from experiments carried out by Graham[1]; these related to a phenomenon which he called *transpiration*, viz. the slow flow through a long, fine capillary tube, or through a bundle of such tubes, or finally through the fine pores of a porous substance. The theory of these experiments, which are obviously similar to those carried out by Poiseuille[2] and Hagen[3] on the behaviour of water and other liquids in passing through a capillary tube, may be easily developed by the analogy of the theory of these hydraulic experiments worked out by Stokes[4] and others, now that the independence of the viscosity of air on pressure has been rendered at least very probable; for, in spite of the variation of pressure along the tube through which the flow takes place, the friction exerted may be assumed to be the same everywhere. This theory, which I published in a second memoir,[5] led in the case of gases to a law of speed of flow which corresponds fully with that found by Poiseuille for liquids, and, like the latter, can be used to calculate the numerical value of the coefficient of viscosity from the measured amount of the gas transpired. Since the deduction of this law rests on the hypothesis of a friction which is not variable with the pressure, an experimental confirmation of it is also a proof of the correctness of the hypothesis. This confirmation was actually given by the experiments, as the following numbers show, provided that the tubes used in the experiments were sufficiently long.

The following table[6] contains the calculation of the results given by Graham in his tables XV. and XVI. Here $t$ denotes the time in seconds required for the flow of a given volume of gas, and $P$ the excess of pressure in inches which causes the flow; $D$ is an auxiliary quantity, proportional to the viscosity-coefficient $\eta$, which is used in the calculation, and is constant like that coefficient; the added values of $\eta$, referred to centimetres and seconds as units, have been calculated from the mean values of $D$. $\mathfrak{L}$ is the length of the transpiration tube in inches.

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[1] *Phil. Trans.* 1846, cxxxvi. p. 573; 1849, cxxxix. p. 349.

[2] *Soc. Philomath.* 1838, p. 77; *Comptes rendus*, 1840, xi. pp 961, 1041; 1841, xii. p. 112; *Ann. Chim.* [3] 1843, vii. p. 50; 1847, xxi. 76; *Mém. de Savants Etrangers*, 1846, ix. p. 433.

[3] *Pogg. Ann.* 1839, xlvi. p. 423; *Abh. d. Berl. Akad.* 1854, p. 17.

[4] *Cambridge Phil. Trans.* 1851–6, ix. pt. 2, p. 8.

[5] *Pogg. Ann.* 1866, cxxvii. pp. 253, 353.

[6] *Ibid.* 1866, cxxvii. pp. 279, 365. In this memoir I have given a slightly different meaning to these numbers; this, however, has no influence on the meaning now assigned.

| $\mathfrak{L}$ | $P$ | Air | | Oxygen | | Hydrogen | |
|---|---|---|---|---|---|---|---|
| | | $t$ | $D$ | $t$ | $D$ | $t$ | $D$ |
| 2 | 20 | 211·5 | 20·12 | 234·0 | 22·26 | 101·7 | 9·68 |
| | 12 | 465·5 | 19·89 | 515·3 | 22·01 | 226·0 | 9·65 |
| | 8 | 642·0 | 19·80 | 711·7 | 21·96 | 314·0 | 9·68 |
| | 4 | 922·5 | 19·78 | 1032·5 | 22·14 | 453·7 | 9·73 |
| | 2 | 1195·0 | 19·89 | 1334·0 | 22·20 | 597·2 | 9·94 |
| | | Mean | 19·90 | Mean | 22·11 | Mean | 9·74 |
| | | $\eta$ = 0·000177 | | $\eta$ = 0·000197 | | $\eta$ = 0·000087 | |
| 4 | 20 | 418·0 | 19·88 | 467 | 22·26 | | |
| | 12 | 930·0 | 19·86 | 1042 | 22·25 | | |
| | 8 | 1290·5 | 19·90 | 1445 | 22·30 | | |
| | 4 | 1865·5 | 20·00 | 2093 | 22·39 | | |
| | 2 | 2436·0 | 20·27 | 2752 | 22·90 | | |
| | | Mean | 19·98 | Mean | 22·37 | | |
| | | $\eta$ = 0·000178 | | $\eta$ = 0·000199 | | | |

Other series of experiments show an equally excellent agreement, but unfortunately the calculation of the viscosity-coefficients cannot be made in absolute measure from the results given.[1]

Simultaneously with this second memoir of mine there appeared, as has already been indicated, a paper by Maxwell[2] himself, in which he too brought forward experimental proof of the independence of the friction on the pressure by use of a method like Coulomb's. Maxwell's apparatus differs from mine by an improvement that is apparently only slight, but in reality is extremely important.[1] Between the three oscillating discs fixed to a common axis, as well as above and below them, Maxwell placed four fixed discs at distances from them that were everywhere the same and as little as possible. The first effect of this is to cause the friction of the air to exert on the oscillating discs a greater resistance, and one therefore more easily measured. A second advantage of Maxwell's method consists in the mathematical theory leading to a final formula which gives the viscosity-coefficient directly, while mine led first of all to the square root of the coefficient, to a magnitude, that is, the error of which would be doubled on squaring. For these reasons Maxwell's numbers show the constancy of the coefficient of viscosity much better than mine. The following table contains the mean values given in the much fuller table[2] drawn up by him. The values of the pressures are given in inches of mercury, and opposite each value of the observed logarithmic decrement is put the corresponding value which is calculated on the assumption of the constancy of the coefficient of viscosity :—

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[1] The remarkable slowness with which, according to the numbers published, air and other gases flow through narrow tubes has called a remark from Stefan (*Wiener Sitzungsber.* 1874, lxix. p. 713), which, though of no further importance for our theory, deserves mention. The adhesion of flat plates together is only an apparent attraction; the cause of the phenomenon is the slowness with which the air penetrates into the narrow interval between the plates; they hang therefore together for a long time by reason of the pressure exerted by the air on their external surfaces.

[2] *Proc. Roy. Soc.* 1866, xv. p. 14; *Phil. Trans.* 1866, clvi. p. 249.

| Pressure | Logarithmic decrement | |
|---|---|---|
| | Observed | Calculated |
| 0·54 | 0·157 | 0·156 |
| 5·68 | 0·156 | 0·156 |
| 20·09 | 0·152 | 0·153 |
| 29·29 | 0·153 | 0·154 |

The agreement of these numbers proves the correctness of the law required by the kinetic theory, viz. that *the coefficient of viscosity of air is independent of its pressure* within *the limits of pressure from* 1 *to* $\frac{1}{60}$ *atmosphere.*

Maxwell further experimented on the friction of hydrogen and carbonic acid. For a great number of other gases a similarity of behaviour was proved by the transpiration experiments of Graham on the one hand, and of Springmühl and myself[1] (which were made later) on the other; such proof being founded on the law discovered by Graham, that the times in which two different gases flow through a tube under the same circumstances have always the same ratio.

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[1] See my memoir on this method (*Pogg. Ann.* 1871, cxliii. p. 14).

[2] *Phil. Trans.* 1866, clvi. p. 266, Table IV.

After all these researches it still remains undecided whether Maxwell's law of the constancy of the coefficient of friction still holds at very small pressures of the gas, or to what extent of rarefaction the law may be considered valid. That it cannot hold right down to the limit zero has already (§ 76) been pointed out. We may therefore expect that deviations from it will be exhibited when the pressure is only a few millimetres of mercury, or when it is lowered so exceedingly far as in the Geissler's tubes used for electro-optical experiments by Plücker, Hittorf, and Crookes.

A first attempt to decide this question was made by Kundt and Warburg,[2] who repeated Maxwell's experiments and pursued the phenomenon down to extremely low values of the pressure. Their experiments confirmed Maxwell's result that the law is valid till the pressure falls to $\frac{1}{60}$ atmosphere; but from that point onward they noted a marked diminution in the value of the logarithmic decrement. But they explained this diminution not as a consequence of the coefficient of friction being smaller at such low pressures, but by a considerably increasing effect at low pressures of the slipping of the gas on the discs of the apparatus. We shall return to this point later (§ 83).

That this explanation is correct, and that the coefficient of viscosity really remains constant, as Kundt and Warburg assume, down to extremely small values of the pressure, was proved by Crookes[3] by observations in which he employed a vertically suspended leaf of mica instead of a horizontally oscillating disc. From the oscillations of this leaf he was able, by help of a theory developed by Stokes,[4] to arrive at conclusions with respect to the magnitude of the viscosity of rarefied air without external friction coming into the question, since slip was excluded by this arrangement of the experiment. From these measures it resulted that Maxwell's law of the constancy of the coefficient of viscosity in actual gases holds down to pressures which are so small that they can no longer be measured with accuracy. Only at a much higher rarefaction there occurs a sudden drop in the value of the coefficient of viscosity.

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[1] *Pogg. Ann.* 1873, cxlviii. pp. 1, 526.

[2] *Monatsber. d. Berl. Akad.* 1875, p. 160; *Pogg. Ann.* 1875, clv. pp. 337, 525.

[3] *Phil. Trans.* 1881, clxxii. p. 387.

[4] *Ibid.* 1881, clxxii. p. 435.

Just as at very low pressures, so also at very high pressures, Maxwell's law of the constancy of the viscosity-coefficient loses its strict validity; for under these circumstances, too, the assumptions of the theory no longer hold good. The theory starts with the assumption that a particle of gas traverses a straight length of path between successive encounters with others, in comparison with which the curved parts of the path that are traversed during the actual encounters are vanishingly small. But this assumption can no longer be upheld when the gas is very dense. The dissociation of the molecules also may cause the law to lose its admissibility, for the theory assumes that the molecules are unalterable.

That the law does not hold any longer with exactness at very high or very low pressures cannot form any objection against the validity of the theory under ordinary circumstances, *i.e.* at moderate pressures and average temperatures; and we may for the present leave out of account that at very high pressures the value of the viscosity-coefficient of a gas perceptibly increases with the density, as Warburg and von Babo[1] have shown for carbonic acid at pressures between 30 and 120 atmospheres.

For other gases which conform more exactly to the laws of perfect gases the question has not been sufficiently investigated. For even if the coefficient of viscosity for air and other gases seems, according to many observations,[2] to increase as the pressure rises, yet all these experimental results admit of other explanations as well. We may therefore conclude, as the united testimony of all the observations, that within wide limits of the pressure the internal friction of gases is variable with the pressure either not at all or only in a very slight degree.

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[1] *Ber. d. naturf. Ges. zu Freiburg i. B.* 1882, viii.; *Wied. Ann.* 1882, xvii. p. 390; *Berl. Sitzungsber.* 1882, p. 509. Compare § 89 and the following.

[2] Graham, *Phil. Trans.* 1846 and 1849; *Pogg. Ann.* 1865, cxxvii. pp. 271, 355, and fol. P. Hoffmann, *Wied. Ann.* 1884, xxi. p. 470. Barus, *Bull. of*

## 78. Numerical Values of the Free Path and Collision-frequency of Particles of Air

This confirmation of a predicted fact constitutes a brilliant success for the kinetic theory. We may assure ourselves by it that we are not moving in the doubtful region of hypothesis, but on the sure ground of experiment, when we employ the results that have been thus far obtained to widen our knowledge of the molecular motion and to investigate the direct properties of molecules.

The formula established in § 75 for the coefficient of viscosity of a gas,

$$\eta = \tfrac{1}{3}\rho L G,$$

now that it is justified by experiment, assumes a no smaller importance than the analogous formula

$$p = \tfrac{1}{8}\pi\rho\Omega^2 = \tfrac{1}{3}\rho G^2$$

that holds for the pressure (§§ 11 and 27); for just as we employ the latter to calculate the absolute value of the molecular speed, we can use the former to determine the value of the molecular free path. The formula enables us to calculate in absolute measure the numerical value of this length, which is apparently inaccessible to observation, when the internal friction of a gas measured in absolute units is known and the value of the molecular speed is obtained from the pressure and density.

Before we follow Maxwell in this important step we must point out that the formula for the viscosity is capable of a slight improvement. It was deduced in § 75 by a con-

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*the U.S. Geological Survey, No.* 54, 'Measurement of High Temperatures,' Washington 1889. De Heen, *Bull. de l'Acad. de Belgique*, 1888 [3] xvi. p. 195.

sideration in which for simplicity equal mean values, both of the speed and the free path, were ascribed to all the molecules instead of values which really vary from molecule to molecule. A more exact calculation of the internal friction of gases, carried out in the fourth Mathematical Appendix (§§ 47* and 48*) in accordance with the rules of the calculus of probability, shows that by the simpler calculation the numerical factor of the formula has become affected by a slight error. It is more exact to put

$$\eta = 0{\cdot}30967\ \rho L \Omega$$

for the coefficient of viscosity, where $\Omega$ is the arithmetical mean of the speeds on Maxwell's theory, and

$$L = \lambda^3 / \pi s^2 \sqrt{2}$$

is the mean value of the free path on the same theory (§ 68).

Although atmospheric air is a mixture of molecules of different kinds which have unequal speeds and traverse unequal paths, yet we may apply the theoretical formula to air, if not with exactness, still with approximate admissibility, to calculate the mean free path of its heterogeneous molecules. My transpiration experiments[1] gave for the coefficient of viscosity of air at 0° C. values from

$$\eta = 0{\cdot}000168 \quad \text{to} \quad \eta = 0{\cdot}000174,$$

which, as mentioned already in § 75, are expressed in terms of the centimetre, the density of water, and the second as units. Puluj,[2] from his transpiration experiments, found

$$\eta = 0{\cdot}000179;$$

von Obermayer,[3] also by transpiration experiments by two different methods,

$$\eta = 0{\cdot}000171 \text{ and } 0{\cdot}000168;$$

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[1] Fourth and fifth memoirs on the viscosity of gases. *Pogg. Ann.* 1873, cxlviii. pp. 37, 203.

[2] *Wiener Sitzungsber.* Abth. 2, 1874, lxix. p. 287; lxx. p. 243.

[3] *Carl's Rep. f. Experimentalphysik*, 1876, xii. p. 13; *Wiener Sitzungsber.* Abth. 2, 1875, lxxi. p. 281; 1876, lxxiii. p. 433.

Otto Schumann,[1] by oscillation experiments after Maxwell's method,

$$\eta = 0{\cdot}000168\,;$$

Schneebeli,[2] by transpiration experiments,

$$\eta = 0{\cdot}000171\,;$$

Tomlinson,[3] by oscillation experiments with cylinders,

$$\eta = 0{\cdot}000172.$$

The mean value of all these determinations is

$$\eta = 0{\cdot}000172.$$

If we join with this value, which is referred to centimeters, the value of the mean speed at 0° C., as calculated in § 28, which in centimetres per second is

$$\Omega = 44{,}700,$$

and employ the value of the density of air at 0° C. under the barometric pressure of 76 cm. as given by Regnault, viz.

$$\rho = 0{\cdot}0012932,$$

in grams per cubic centimetre, we find for the mean free path, measured in centimetres, of a particle of air at 0° C. and under the pressure of one atmosphere the value

$$L = 0{\cdot}0000096.$$

From this mean value of the path we obtain, by comparison of it with the length $\Omega$ travelled in a second, the mean number of collisions that occur per second and of the paths that are newly begun in each second, viz.

$$\Omega / L = 4{,}650{,}000{,}000.$$

The two numerical values of the free path and collision-frequency here established on an experimental basis prove, the former by its smallness and the latter by its greatness, how correct was the expectation which Clausius[4] expressed in his refutation of the objections raised against his theory. The molecular free path has indeed come out as a magnitude which is three times smaller than the smallest microscopically visible magnitude[1]; and the vibrations of the air molecules as they course backwards and forwards take place more than 60,000 times more rapidly than those for the highest tone audible.[2]

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[1] *Wied. Ann.* 1884, xxiii. p. 353.

[2] *Archives des Sci. Phys. et Nat. Genève*, 1885 [3] xiv. p. 197.

[3] *Phil. Trans.* 1886, clxxvii. p. 767.

[4] Compare §§ 62 and 72.

## 79. Free Path and Collision-frequency of the Particles of Different Gases

Just as for atmospheric air, the values of the two magnitudes, the free path and the collision-frequency, may be calculated for every other gas for which the value of the coefficient of viscosity has been measured. In place of this it is also sufficient if the particular ratio is known for the gas, which Graham has called the *coefficient of transpiration*, viz. the ratio in which the coefficient of viscosity of the gas stands to that of oxygen. The value of this ratio has been determined for many gases by Graham,[3] by measuring the speed with which the gases flow through fine capillary tubes; the times of flow of equal volumes of different gases are in the same ratio as their coefficients of viscosity. Graham found that the value of this ratio varies only insignificantly with the temperature and pressure, so long as these two magnitudes are not altered too greatly. It is therefore possible, from the mean value that has been found for the coefficient of viscosity of atmospheric air, viz. $\eta = 0{\cdot}000172$, and the transpiration-coefficient for air determined by Graham, viz. 0·899, to at once calculate the coefficient of viscosity of oxygen, viz.

$$\eta = 0{\cdot}000191,$$

and thence the values of the coefficients of viscosity of all the other gases experimented on by Graham. We then find, just as for air, the values of the free path and collision-frequency of the molecules of all these gases.

The results of this calculation are given in the following table. The numbers are referred to the centimetre, the second, and the density of water as units, as were the values for air which underlie them; as, too, in the case of air, they correspond to the temperature 0° C. and the pressure of 76 cm. of mercury. The values of the molecular weights have been taken from the tables of Lothar Meyer and Karl Seubert.[1]

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[1] Helmholtz, *Pogg. Ann.* 1874, Jubelband, p. 575.

[2] Depretz, *Comptes rendus*, 1845, xx.; *Pogg. Ann.* 1845, lxv. p. 447. He gives 37,000 complete, or 74,000 single, oscillations per second as the limit for audibility.

[3] *Phil. Trans.* 1846 and 1849.

| | Molecular | | Coefficient of | | Molecular free path | Collision-frequency |
|---|---|---|---|---|---|---|
| | Formula | Weight | Transpiration | Viscosity | | |
| Hydrogen . . | $H_2$ | 2·00 | 0·439 | 0·000084 | 0·0000178 | 9520 × $10^6$ |
| Marsh gas . . | $CH_4$ | 15·91 | 0·555 | 106 | 080 | 7530 „ |
| Ammonia . . | $NH_3$ | 16·94 | 0·511 | 098 | 071 | 8160 „ |
| Carbon monoxide . | $CO$ | 27·79 | 0·870 | 167 | 095 | 4800 „ |
| Ethylene . . | $C_2H_4$ | 27·82 | 0·516 | 099 | 042 | 8090 „ |
| Nitrogen . . | $N_2$ | 27·88 | 0·873 | 167 | 095 | 4780 „ |
| Nitric oxide . . | $NO$ | 29·82 | 0·878 | 168 | 094 | 4750 „ |
| Oxygen . . | $O_2$ | 31·76 | 1·000 | 191 | 102 | 4180 „ |
| Hydrogen sulphide | $H_2S$ | 33·82 | 0·616 | 118 | 060 | 6780 „ |
| Hydrogen chloride | $HCl$ | 36·19 | 0·736 | 141 | 071 | 5670 „ |
| Carbonic acid . | $CO_2$ | 43·67 | 0·755 | 145 | 065 | 5530 „ |
| Nitrous oxide . | $N_2O$ | 43·76 | 0·752 | 144 | 065 | 5550 „ |
| Methyl ether . | $C_2H_6O$ | 45·70 | 0·483 | 092 | 041 | 8650 „ |
| Methyl chloride . | $CH_3Cl$ | 50·10 | 0·547 | 105 | 044 | 7630 „ |
| Cyanogen . . | $C_2N_2$ | 51·70 | 0·506 | 097 | 040 | 8250 „ |
| Sulphur dioxide . | $SO_2$ | 63·58 | 0·654 | 125 | 047 | 6390 „ |
| Ethyl chloride . | $C_2H_5Cl$ | 64·01 | 0·499 | 095 | 036 | 8370 „ |
| Chlorine . . | $Cl_2$ | 70·38 | 0·666 | 128 | 046 | 6270 „ |

From these numbers of Graham's the determinations of von Obermayer[2] present deviations of no importance; they also refer to the temperature 0° C., and are reduced to absolute measure by direct gauging of the capillary tubes.

| | Molecular | | Coefficient of viscosity | Free path | Collision-frequency |
|---|---|---|---|---|---|
| | Formula | Weight | | | |
| Hydrogen . . | $H_2$ | 2·00 | 0·000086 | 0·0000182 | 9280 × $10^6$ |
| Carbon monoxide | $CO$ | 27·79 | 162 | 092 | 4920 „ |
| Ethylene . . | $C_2H_4$ | 27·82 | 092 | 052 | 8670 „ |
| Nitrogen . . | $N_2$ | 27·88 | 166 | 094 | 4820 „ |
| Oxygen . . | $O_2$ | 31·76 | 187 | 100 | 4280 „ |
| Carbonic acid . | $CO_2$ | 43·67 | 138 | 063 | 5780 „ |
| Nitrous oxide . | $N_2O$ | 43·76 | 135 | 061 | 5910 „ |
| Ethyl chloride . | $C_2H_5Cl$ | 64·01 | 089 | 033 | 8990 „ |

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[1] *Zeitschr. f. anorg. Chemie*, 1896, xiii. 231.

[2] *Wiener Sitzungsber.* Abth. 2, 1875, lxxi. p. 281; 1876, lxxiii. p. 433. *Carl's Repert. f. Experimentalphys.* 1876, xii p. 13; 1877, xiii p. 130.

The values also deduced by Kundt and Warburg[1] from oscillation experiments at 15° C. differ from the former by nothing more than can be explained by the change of temperature.

| | Molecular | | Coefficient of viscosity | Free path | Collision-frequency |
|---|---|---|---|---|---|
| | Formula | Weight | | | |
| Hydrogen . . | $H_2$ | 2·00 | 0·000092 | 0·0000201 | $8430 \times 10^6$ |
| Water vapour . | $H_2O$ | 17·88 | 097[2] | 071 | 7980 ,, |
| Carbonic acid . | $CO_2$ | 43·67 | 152 | 071 | 5120 ,, |

With these numbers the values are in good agreement which Puluj[3] and O. Schumann[4] have deduced from their observations. I must, however, abstain from citing here all the determinations that have been made, but will mention those measures that concern the newly discovered gases argon and helium, and that have been made with the vapour of mercury.

The transpiration-coefficients of both these gases have been determined by Lord Rayleigh[5]; he found the values 1·21 for argon and 0·96 for helium referred to air. Thence, taking 0·000172 as the viscosity-coefficient for air, we obtain for

argon, 0·000208,
helium, 0·000165

as the value of the coefficient of viscosity at 0°, the temperature for which that of air is given.

Before we can calculate the free paths from these values we must calculate also the molecular speed, for which the values of the specific gravities are required. The density of argon is given by Rayleigh as bearing to that of oxygen the ratio 3·2746 : 2·6276, whence, by use of the numbers given in § 28, I calculate the density of argon at 0°, referred to that of water at 4° C., as

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[1] *Pogg. Ann.* 1875, clv. p. 540.

[2] Houdaille (*Fortsch. d. Phy.* 1896, 52. Jahrg. i. p. 442) finds the coefficient of viscosity of water vapour to be much smaller at low pressures, probably as a consequence of dissociation (§ 89).

[3] *Wiener Sitzungsber.* 1876, lxxiii. Abth. 2, p. 589; *Carl's Repert. f. Experimentalphys.* 1877, xiii. p. 293.

[4] *Wied. Ann.* 1884, xxiii. p. 353.

[5] *Proc. Roy. Soc.* 1896, lix. p. 198; *Zeitschr. f. phys. Chemie*, 1896, xix. p. 364.

$$\rho = 0{\cdot}0017810,$$

whence the mean speed at 0° of the molecule of argon is

$$\Omega = 381 \text{ metres per sec.}$$

For helium the numbers are somewhat uncertain; in the mean Ramsay[1] found the value 2·14 for the density when that of oxygen was taken as 16. Hence follows, when the density is referred to that of water,

$$\rho = 0{\cdot}000191,$$

for which the mean speed at 0° is

$$\Omega = 1162 \text{ metres per sec.}$$

From these numbers we obtain then the molecular free paths,

for argon, 0·0000099 cm.,
for helium, 0·0000240 ,,

at 0° and atmospheric pressure, and, finally, the collision-frequency of a molecule

for argon, $3840 \times 10^6$ per sec.,
for helium, 4840 ,, ,,

The viscosity of mercury vapour has been measured by S. Koch,[2] and the numbers found by him have later been confirmed as correct by Noyes and Goodwin[3] by means of comparative transpiration experiments. At the temperature 370° C. the value of the coefficient of viscosity was found to be

$$\eta = 0{\cdot}000642,$$

while according to the numbers given in § 28 the value of the molecular speed at this temperature must be taken as

$$\Omega = 260 \text{ metres per sec.}$$

Hence from the formula

$$L = \tfrac{1}{3}\pi\eta\Omega / 0{\cdot}30967\, p$$

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[1] *Proc. Roy. Soc.* 1896, lix. p. 325; *Zeitschr. f. phys. Chemie*, 1896, xx. p. 614.

[2] *Wied. Ann.* 1883, xix. p. 857.

[3] *Zeitschr. f. phys. Chemie*, 1896, xxi. p. 671; *Phys. Rev.* 1896, iv. p. 207.

the value of the free path of mercury vapour at 370° C. and atmospheric pressure is

$$L = 0{\cdot}0000209 \text{ cm.},$$

and that of the collision-frequency under the same circumstances

$$\Omega / L = 1245 \times 10^6 \text{ per sec.}$$

An estimation of the values at 0° can only be made with great uncertainty, since the law of alteration of $\eta$ with temperature at such low temperatures is not known. If we employ the formula of interpolation determined by Koch for high temperatures, according to which $\eta$ is proportional to the 1·6th power of the absolute temperature, and put $\Omega$ proportional to the square root of the same magnitude, we have for mercury vapour at 0° and atmospheric pressure

$$\eta = 0{\cdot}000162,\ L = 0{\cdot}00000344,\ \Omega / L = 7540 \times 10^6.$$

We may expect that in the foregoing series of numbers regular relations between the free paths and molecular weights may be recognisable. For it can scarcely appear doubtful that the area of the central section of the sphere of action which is contained in the formula for the free path is closely connected with the molecular volume; and it is just as probable that the molecular volume depends in like manner on the molecular weight, as in chemically simple bodies the atomic volume depends on the atomic weight. But Lothar Meyer[1] has shown that, as the atomic weight increases, the atomic volume now increases, now decreases, with a peculiar kind of double periodicity; and similar behaviour has been shown, by the investigations of Mendelejeff, Lothar Meyer, and other chemists, in the case of all other physical properties of the chemical elements. Consequently we may expect that the molecular free path and collision-frequency will also be functions of the molecular weight that regularly decrease and increase.

Graham has already recognised the simplest relations to the molecular weight. He noticed that substances of equal molecular weight in many cases possess the same coefficient of transpiration, in consequence of which they must also have the same free path and collision-frequency. This rule, however, does not hold in general, but only for such substances whose molecules are made up of the same number of atoms. Thus, for instance, CO, $N_2$, and NO, which all three have two atoms in the molecule, have nearly equal free paths and collision-frequencies in addition to nearly equal molecular weights, while the molecule $C_2H_4$, consisting of six atoms, shows a much smaller free path and a much larger collision-frequency, although it has the same molecular weight. Further, the molecules $CO_2$ and $N_2O$, composed of three atoms, agree in respect of weight, viscosity, free path, and collision-frequency, while the only slightly heavier molecule $C_2H_6O$, consisting of nine atoms, has a much smaller viscosity and free path, and a much larger collision-frequency. In both these cases, therefore, the collision-frequency is the greater the more atoms in the molecule.

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[1] *Ann. d. Chem. u. Pharm.* 1870, Suppl.-Band vii. p. 354.

If now we arrange the substances enumerated according to the number of atoms in the molecule, we first obtain the following two series, whose regularity is obvious :—

| Number of atoms in molecule | Molecular | | Coefficient of viscosity | Free path | Collision-frequency |
|---|---|---|---|---|---|
| | Formula | Weight | | | |
| 2 | $H_2$ | 2·00 | 0·000084 | 0·0000178 | 9520 × $10^6$ |
| | CO | 27·79 | 167 | 095 | 4800 „ |
| | $N_2$ | 27·88 | 167 | 095 | 4780 „ |
| | NO | 29·82 | 168 | 094 | 4750 „ |
| | $O_2$ | 31·76 | 191 | 102 | 4180 „ |
| | HCl | 36·19 | 141 | 071 | 5670 „ |
| | $Cl_2$ | 70·38 | 128 | 046 | 6270 „ |
| 3 | $H_2O$ | 17·88 | 0·000097 | 0·0000071 | 7980 × $10^6$ |
| | $H_2S$ | 33·82 | 118 | 060 | 6780 „ |
| | $CO_2$ | 43·67 | 145 | 065 | 5530 „ |
| | $N_2O$ | 43·76 | 144 | 065 | 5550 „ |
| | $SO_2$ | 63·58 | 125 | 047 | 6390 „ |

The numbers here tabulated confirm our expectation so far as to show that *the values of the coefficient of friction, free path, and collision-frequency within each group now rise and now fall in a periodic way while the molecular weight increases.*

The periodicity is exhibited most clearly in the first group, which embraces the diatomic molecules; it is repeated, however, in the same way, but less markedly, in the second group, which contains the triatomic molecules. *In both groups as the molecular weight rises, the coefficient of viscosity so alters as to first of all rise, and then fall after having attained a maximum. The free path diminishes in both groups at first, then undergoes a slight increase, and finally diminishes again. Lastly, the collision-frequency falls off at first to a minimum, and then increases.*

Whether these relations hold good with monatomic molecules can scarcely be judged from the numbers at hand. To this class of gases belong not only mercury vapour, but also argon and helium, because both these gases, in common with mercury, have this property, that for them the ratio of the two specific heats has the value[1] 1·67 (§ 54). We should then have to tabulate the following numbers calculated for 0° C.:—

| Number of atoms in molecule | Molecular |  | Coefficient of viscosity | Free path | Collision-frequency |
|---|---|---|---|---|---|
|  | Formula | Weight |  |  |  |
| 1 | He | 4·3 | 0·000165 | 0·0000240 | $4840 \times 10^6$ |
|  | A | 39·5 | 208 | 099 | 3840 „ |
|  | Hg | 198·8 | 162 | 344 | 7540 „ |

Of these the values of the coefficient of viscosity and the collision-frequency exhibit the behaviour described, but not the values of the free path.[2] We must not, however, forget that the credibility of the foregoing figures is open to sundry objections, and especially because the variation of the viscosity of mercury vapour with the temperature has not been determined with sufficient certainty. On the other hand, doubts have been often expressed whether argon and helium are really simple substances, and not, perhaps, mixtures, and whether the molecule of argon has really only one atom, and not perhaps two or three. In the first two tables, however, for diatomic and triatomic molecules the numbers determined for argon fit in much less well.

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[1] *Proc. Roy. Soc.* 1895; *Zeitschr. f. phys. Chemie*, 1895, xvi. p. 363; *Journ. Chem. Soc.* 1895, lxvii. p. 684; *Wied. Beibl.* xix. p. 674.

[2] [The values for *three* gases only cannot show more than is shown above.—Tr.]

For gases which have more than three atoms in the molecule the foregoing numbers permit of just as little certainty with respect to a regular dependence on the molecular weight. A difficulty which specially arises is that, as the following table shows, the differences between the values of the viscosity-coefficient and of the magnitudes deduced from it become the smaller the higher the number of atoms in the molecule.

| Number of atoms in molecule | Molecular | | Coefficient of viscosity | Free path | Collision-frequency |
|---|---|---|---|---|---|
| | Formula | Weight | | | |
| 4 | $NH_3$ | 16·94 | 0·000098 | 0·0000071 | 8160 × $10^6$ |
| 4 | $C_2N_2$ | 51·70 | 097 | 040 | 8250 ,, |
| 5 | $CH_4$ | 15·91 | 106 | 080 | 7530 ,, |
| 5 | $CH_3Cl$ | 50·10 | 105 | 044 | 7630 ,, |
| 6 | $C_2H_4$ | 27·82 | 099 | 042 | 8090 ,, |
| 8 | $C_2H_5Cl$ | 64·01 | 095 | 036 | 8370 ,, |
| 9 | $C_2H_6O$ | 45·70 | 092 | 041 | 8650 ,, |

The explanation of the relations described is, on the whole, not difficult to give from the theoretical formula for the free path,

$$L = \lambda^3 / \pi s^2 \sqrt{2},$$

according to which it appears as a magnitude which is not directly dependent on the mass $m$ of the molecule, but only on the occupation of space by a molecule. It is therefore variable with the molecular weight only in so far as the space-occupation depends upon it. But this enters into the formula in two ways, both in the numerator and in the denominator. The volume $\lambda^3$ of the elemental cube, *i.e.* of that part of space which contains just one molecule (§ 63), occurs in the numerator; but this, according to Avogadro's law (§ 31), is the same for all gases when they are at the same pressure and temperature. Only the denominator, therefore, in the formula for the free path, that is, only the area $\pi s^2$ of the central section of the sphere of action, is variable with the molecular weight. With respect to this section we may in general suppose that it increases with the molecular weight, and also with the number of atoms which are joined together in the molecule.

This supposition is also actually justified by the numbers given as values of the free path for diatomic and triatomic molecules; for on the whole they decrease as the molecular weight increases, and they are on the average smaller for triatomic molecules than for diatomic.

Yet in each of these two series of values of the free path there occurs about the middle a slightly marked but still plainly recognisable rise. The central section, therefore, of the sphere of action cannot continuously increase as the molecular weight increases, but at mean values of the molecular weight the section must decrease when the weight increases. This behaviour is explained the most simply if we assume that the atoms in the molecule can be grouped together differently, and we may indeed assume that they draw the more closely together the heavier their masses. The consequence of this would be that with increase of mass the sphere of action is contracted, although the intensity of the action will perhaps increase.

After this discussion the relations between the numbers that represent the collision-frequency are easily intelligible. The formula for the collision-frequency is

$$1/T = \Omega/L = \sqrt{2}\pi s^2 \Omega/\lambda^3;$$

this contains a factor $\Omega$, which continuously decreases as the molecular weight increases, while the other factor $\pi s^2$ for the most part increases with the molecular weight. The collision-frequency may therefore as well decrease as increase with increase of the molecular weight.

According to the formula a greater value of the collision-frequency may result from two different causes which are, to a certain extent, antagonistic. On the one hand this number is increased by an increase in the speed of the particles, on the other it rises in value with the extent of the sphere of action, and therefore with the mass of the molecule. Consequently those molecules collide the oftenest which, firstly, move with the greatest rapidity, that is, the lightest; and those, secondly, which are in a certain measure heavy by reason of their mass and extent. With this the run of the numbers agrees; the collision-frequency first diminishes, and then increases, as the molecular weight increases.

An exactly similar explanation serves to account for the observation that gaseous chemical compounds which are polyatomic behave nearly alike as regards viscosity, and indeed we see this just as before from the mathematical expression for the collision-frequency. By the entrance of more atoms into the molecule the section $\pi s^2$ will in most cases increase, while the molecular speed will diminish; the interval $T$ between successive collisions may therefore be constant. In this case the coefficient of viscosity must also be constant; for the formula which gives it,

$$\eta = 0{\cdot}30967\, \rho L \Omega,$$

leads to the relation

$$\eta / T = 0{\cdot}30967\, \rho \Omega^2$$

between the viscosity and the collision-interval $T$, and by substitution of the pressure by means of the formula $p = \frac{1}{8}\pi\rho\Omega^2$ we can bring this into the form

$$\eta / T = 0{\cdot}03871\, \pi p = 0{\cdot}121607\, p.$$

If therefore $T$ is independent of the molecular weight, so too is $\eta$. Hence *all gaseous substances which contain a large number of atoms in their molecule have nearly equal coefficients of viscosity.*

This law is important in the examination of the behaviour of vapours, which we have still to investigate (§ 86). But we must first discuss some other relations which there come into consideration.

## 80. Viscosity of Gaseous Mixtures

Both theory and experiment agree in showing that the principal laws of viscosity hold not only for chemically pure gases, but also for mixtures of different gases. Indeed, it is a mixed gas, atmospheric air to wit, which has been employed by most observers much oftener than pure gases to prove the independence of the viscosity on the pressure and to investigate its dependence on the temperature.

The theoretical considerations retain their validity also for mixed gases, especially the deduction given in § 75 of the formula which expresses the theoretical value of the coefficient of viscosity. In this reasoning mean values were always dealt with; the mean momentum which is carried by the moving particles in unit time over unit area in a given direction was brought into account, and also the mean value of the distance which is traversed by the particles that cross the area. From the two we obtained the amount of the friction which in a particular case is equal to the coefficient of viscosity. This calculation, depending on mean values, does not in any way assume equality of all the molecules; for mean values of magnitudes that have even very unequal values can be formed. The fundamental formula of the theory is therefore valid also for gaseous mixtures; the question now only arises how to form the necessary mean values.

We can attempt this in different ways. We may either direct our efforts to the carrying out of the mathematical calculation as strictly as possible, and so far as is possible without neglecting anything, or strive to find simpler formulæ, which are easy to evaluate for numerical calculations. Maxwell[1] has followed the first way; here we employ an easier method, which is due to Puluj.[2]

The formula for the coefficient of viscosity

$$\eta = 0{\cdot}30967\ \rho\Omega\lambda^3/\pi s^2\sqrt{2}$$

we use for a gaseous mixture in the form

$$\eta = 0{\cdot}30967\ m\Omega/\pi s^2\sqrt{2},$$

where $m$ is the molecular weight, and we thereby understand $m$, $\Omega$, and $s$ as representing mean values. If the mixture of two gases whose molecular weights are $m_1$ and $m_2$ contain $N_1$ and $N_2$ molecules of them respectively in unit volume, the mean value of the molecular weight is

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[1] *Phil. Mag.* 1868 [4] xxxv. p. 212; *Scientific Papers*, ii. p. 72.

[2] *Wiener Sitzungsber.* 1879, lxxix. Abth. 2, pp. 97, 745; *Carl's Repert. d. Experimentalphys.* xv. p. 590.

$$m \equiv (m_1 N_1 + m_2 N_2) / N$$

where
$$N \equiv N_1 + N_2.$$

By means of this mean value $m$ the mean value of the speed $\Omega$ is at once obtainable from the two magnitudes $\Omega_1$, $\Omega_2$ which denote the mean speeds of the two kinds of particles; for there must be equilibrium of temperature, and therefore

$$m\Omega^2 = m_1 {\Omega_1}^2 = m_2 {\Omega_2}^2,$$

whence for the factor $m\Omega$ in the numerator of the expression for $\eta$ we may put

$$m\Omega = m_1 \Omega_1 \sqrt{(m/m_1)} = m_1 \Omega_1 \sqrt{(N_1/N + N_2 m_2 / N m_1)}.$$

Similarly we may alter the denominator. If we put $s_1$ and $s_2$ for the radius of the sphere of action of the two kinds of molecules, the mean volume of the spheres of action is

$$\tfrac{4}{3}\pi s^3 = (\tfrac{4}{3}\pi {s_1}^3 N_1 + \tfrac{4}{3}\pi {s_2}^3 N_2) / N,$$

and therefore the mean central section of the sphere of action is

$$\begin{aligned} \pi s^2 &= \pi \left\{ (N_1 {s_1}^3 + N_2 {s_2}^3) / N \right\}^{\frac{2}{3}} \\ &= \pi {s_1}^2 (N_1/N + N_2 {s_2}^3 / N {s_1}^3)^{\frac{2}{3}}. \end{aligned}$$

Replacing the ratio of $s_2$ to $s_1$ in terms of the viscosity-coefficients from the formulæ

$$\eta_1 = 0{\cdot}30967\; m_1 \Omega_1 / \pi {s_1}^2 \sqrt{2}, \quad \eta_2 = 0{\cdot}30967\; m_2 \Omega_2 / \pi {s_2}^2 \sqrt{2},$$

whence we obtain

$$\left(\frac{s_2}{s_1}\right)^2 = \frac{\eta_1 m_2 \Omega_2}{\eta_2 m_1 \Omega_1} = \frac{\eta_1}{\eta_2}\left(\frac{m_2}{m_1}\right)^{\frac{1}{2}},$$

we have for the mean section

$$\pi s^2 = \pi {s_1}^2 \left\{ \frac{N_1}{N} + \frac{N_2}{N}\left(\frac{\eta_1}{\eta_2}\right)^{\frac{3}{2}} \left(\frac{m_2}{m_1}\right)^{\frac{3}{4}} \right\}^{\frac{2}{3}}.$$

If we put these two mean values in the numerator and denominator of the formula for $\eta$, we obtain for the coefficient of viscosity of the mixed gases the expression

$$\eta = \eta_1 \frac{\left(\frac{N_1}{N} + \frac{N_2}{N}\frac{m_2}{m_1}\right)^{\frac{1}{2}}}{\left\{\frac{N_1}{N} + \frac{N_2}{N}\left(\frac{\eta_1}{\eta_2}\right)^{\frac{3}{2}}\left(\frac{m_2}{m_1}\right)^{\frac{3}{4}}\right\}^{\frac{2}{3}}}.$$

In this formula, however, the numbers $N$ which are not accessible to direct observation may be replaced by the values of the pressure, on the assumption that the mixed gases obey Boyle's and Avogadro's laws. Denoting by $p_1$ the pressure which the first gas, consisting of the molecules $m_1$, would exert by itself, and by $p_2$ that which the second gas alone would produce, and lastly by $p$ the whole pressure exerted by the mixture, which in accordance with Dalton's law is given by

$$p = p_1 + p_2,$$

the formulæ

$$N_1 : N = p_1 : p \quad \text{and} \quad N_2 : N = p_2 : p$$

hold good, and by these the expression for the coefficient of viscosity takes the form

$$\eta = \eta_1 \frac{\left(\frac{p_1}{p} + \frac{p_2}{p}\frac{m_2}{m_1}\right)}{\left\{\frac{p_1}{p} + \frac{p_2}{p}\left(\frac{\eta_1}{\eta_2}\right)^{\frac{3}{2}}\left(\frac{m_2}{m_1}\right)^{\frac{3}{4}}\right\}^{\frac{2}{3}}}.$$

Puluj has made measurements of the internal friction of mixtures of carbonic acid and hydrogen, has compared his results with the formula, and has found a really good agreement. So, too, has Breitenbach.[1] By these observations a striking fact was confirmed, which was first noticed by Graham[2] as he allowed mixtures of hydrogen with other gases to flow through capillary tubes. Although the viscosity of hydrogen is less than that of carbonic acid, a slight admixture of hydrogen has the effect of increasing and not of decreasing the viscosity of carbonic acid; nor does a diminution begin until the mixture contains a largish amount of hydrogen.

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[1] *Wied. Ann.* 1899, lxvii. p. 820.

[2] *Phil. Trans.* 1846, p. 622.

To explain this remarkable phenomenon by the formula, we note that the numerator of the fraction may be put

$$\sqrt{\left(\frac{p_1}{p}+\frac{p_2}{p}\frac{m_2}{m_1}\right)}=\sqrt{\left\{1-\left(1-\frac{m_2}{m_1}\right)\frac{p_2}{p}\right\}}$$

$$=1-\frac{1}{2}\left(1-\frac{m_2}{m_1}\right)\frac{p_2}{p}-\ldots=1-0{\cdot}48\frac{p_2}{p}-\ldots$$

in the case under consideration, where $m_2 = 2$ and $m_1 = 43{\cdot}67$ if $p_2$ is the pressure of the hydrogen, while the denominator becomes

$$\left\{\frac{p_1}{p}+\frac{p_2}{p}\left(\frac{\eta_1}{\eta_2}\right)^{\frac{3}{2}}\left(\frac{m_2}{m_1}\right)^{\frac{3}{4}}\right\}^{\frac{2}{3}}=\left[1-\left\{1-\left(\frac{\eta_1}{\eta_2}\right)^{\frac{3}{2}}\left(\frac{m_2}{m_1}\right)^{\frac{3}{4}}\right\}\frac{p_2}{p}\right]^{\frac{2}{3}}$$

$$=1-\frac{2}{3}\left\{1-\left(\frac{\eta_1}{\eta_2}\right)^{\frac{3}{2}}\left(\frac{m_2}{m_1}\right)^{\frac{3}{4}}\right\}\frac{p_2}{p}-\ldots=1-0{\cdot}52\frac{p_2}{p}-\ldots$$

if the values of the coefficients of viscosity are put in from § 79. For small values of $p_2$, therefore, the numerator diminishes less than the denominator as $p_2$ increases, and the value of $\eta$ must therefore rise in magnitude, and not fall, with increase of $p_2$, so long as this remains small. For larger values of $p_2$ the relation alters.[1]

We may not, therefore, as this instance shows, without further consideration conclude that, because the viscosity of air is greater than that of carbonic acid, the coefficient of viscosity of carbonic acid is increased by the mixture with it of some atmospheric air. But if we put in the formula $m_2 = 28{\cdot}69$ for air (which we assume as a mean value from $N_2 = 27{\cdot}88$ and $O_2 = 31{\cdot}76$), and also $\eta_2 = 0{\cdot}000172$ for air, and $\eta_1 = 0{\cdot}000145$ for carbonic acid, the formula becomes

$$\eta=\eta_1(1-0{\cdot}17\,p_2/p-\ldots)/(1-0{\cdot}29\,p_2/p-\ldots),$$

and from this it follows that $\eta$ increases with $p_2$, and therefore with the amount of added air, even for small values of $p_2$, as Warburg and von Babo[2] have actually observed.[3]

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[1] [The numerator of the fraction is greater in this case than the denominator so long as the ratio $p_2/p$ does not exceed 0·615.—Tr.]

[2] *Ber. über d. Verh. d. naturf. Ges. in Freiburg i. B.* 1882, viii. p. 117; *Wied. Ann.* 1882, xvii. p. 422.

[3] [This behaviour is independent of the relative amounts of the two gases;

Now that the formula has been confirmed, let us, as a simple application of it, calculate the transpiration-coefficient of atmospheric air, that is, the ratio of its coefficient of viscosity $\eta$ to that of oxygen $\eta_1$. Putting $p_1/p = 0{\cdot}21$ and $p_2/p = 0{\cdot}79$, in accordance with the known ratio of mixture of oxygen and nitrogen in air, and also $m_1 = 31{\cdot}76$ for oxygen and $m_2 = 27{\cdot}88$ for nitrogen, and lastly, Graham's value $\eta_2/\eta_1 = 0{\cdot}873$ for the transpiration-coefficient of nitrogen, we obtain for the transpiration-coefficient of atmospheric air

$$\eta/\eta_1 = 0{\cdot}898,$$

which is in complete agreement with the mean value obtained from Graham's observations, viz. 0·899.

## 81. Friction of Gases on Fixed Bodies

A gas experiences frictional effects, not only when two of its layers flow by each other with different speeds, but also when it streams along the surface of a fixed body, or of a body which moves within it; this friction causes the more quickly moving part to be retarded, and the more slowly moving part to be accelerated. This *external friction of gases* has been investigated and measured by Kundt and Warburg.[1]

The existence of a friction between a gas and a solid body assumes that they are moving unequally fast, so that the gas does not adhere firmly to the solid surface, but slips along it. The friction, which diminishes the difference of the velocities by accelerating the slower and retarding the quicker, diminishes this slip on the surface, so that only with very weak or moderately strong external friction is a sensible slip perceptible, while with more considerable friction it almost disappears, and at last entirely ceases. On the other hand, the amount of slip depends also on the magnitude of the internal friction. The stronger this is, the

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for the numerator and denominator are equal only when $p_2/p = 2{\cdot}664$, which does not correspond to any possible combination.—Tr.]

[1] *Pogg. Ann.* 1875, clv. pp. 337, 525. Previously published in abstract in *Monatsber. d. Berl. Akad.* 1875, p. 160.

more the differences of the velocity of flow in the different layers are blotted out, by which the difference between the velocity of the gas, moving as a more compact mass, and that of the solid body must necessarily be increased. The slip therefore increases with increase of internal friction just as with decrease of external friction, while it would be diminished as well by decrease of the internal as by increase of the external friction.

A measure for the amount of the external friction we might obtain in the same way as that for internal friction, viz. by means of a *coefficient of friction*, which measures the intensity of the friction exerted per unit area of the surface if the difference of the two velocities is the unit of velocity. But after our explanation of the relation between friction and slip another method commends itself as no less convenient, viz. to introduce instead, as a measure of the slip, a *coefficient of slip*, as Helmholtz and von Pietrowski[1] have first defined it for liquids. By the coefficient of slip, which we denote by $\zeta$, is understood the ratio of $\eta$, the coefficient of internal friction, to $\varepsilon$, the coefficient of external friction, or

$$\zeta \equiv \eta / \varepsilon,$$

so that $\zeta$ appears a really suitable measure of the slip which is increased by increase of $\eta$ and diminution of $\varepsilon$.

The older investigations of the friction of gases, both those founded on observations of oscillations and those directed to the measurement of transpiration, had agreed in showing that the value of the coefficient of slip is vanishingly small, so that $\zeta$ might be put equal to 0. The external friction, therefore, in the circumstances under which those experiments were carried out, is infinitely greater than the internal. An essential advantage was in consequence gained for the determination of the internal friction, since, as no slip occurred, the external friction might be left out of account in the working out of the observations.

But when Kundt and Warburg undertook to test

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[1] *Wiener Sitzungsber.* 1860, xl. p. 607.

Maxwell's law of the independence of the viscosity on the density for very great rarefactions, such as are to be attained by a mercury pump, they found the external friction considerably lessened in gases rarefied so far, so that the coefficient of slip $\zeta$ could no longer be put equal to 0, and the slip could no longer be neglected. From their experiments, which were carried out at pressures between 0·6 and 20 millimetres of mercury, it resulted that *the value of the coefficient of slip is inversely proportional to the density of the gas. The external friction is consequently directly proportional to the density.* We cannot, after this experiment, conclude from the law found for viscosity by Maxwell that a gas of vanishingly small density would exert the same friction on the motion of a body as a denser gas; the influence of the friction will rather become less as the rarefaction of the gas increases, not indeed by reason of the internal friction diminishing, but because the external friction decreases.

### 82. Theory of External Friction

Kundt and Warburg have already explained by the kinetic theory the law empirically found for the coefficient of slip, in so far as they have shown that on this theory $\zeta$ is a magnitude which is proportional to the free path and, therefore, inversely proportional to the density. But, apparently because a calculation founded on erroneous assumptions did not lead to the correct value of the numerical coefficient of the formula, they have not evaluated their observations on external friction in a complete manner for comparison with the absolute magnitude of the free paths.

The external friction which a gas in flow undergoes at a fixed wall may be calculated just as in § 11 we calculated the pressure which it exerts on the wall. Just as in that case, we have to find the number of particles which meet the wall during unit time, say, one second, in consequence of their molecular motion; each of them loses a portion of its forward velocity by its collision against the fixed wall; the sum of the momenta which the impinging particles lose in a second gives the amount of the friction which the surface-layer of the gas has experienced at the wall.

But to form this sum we have to make a hypothetical assumption as to the magnitude of the loss which a single particle suffers on impact at the wall. In the case carried out in § 11 we supposed that no kinetic energy was lost on the collision, but that the particle was reflected from the wall with the same speed as that with which it struck it. We could not now consistently suppose that the particles of gas lose any of their speed; but we might assert that of the *forward* motion, which all the molecules in common possess, a part must be transformed into *heat*-motion in consequence of the divergency of the directions in which the impinging particles are reflected. How large a part this will be depends on the degree of unevenness of the surface, with respect to which, therefore, we have to form a definite conception.

The fixed wall on which the particles impinge does not form a plane or continuously curved surface at all; it is made up itself of molecules which leave spaces between each other of sufficient size to allow other molecules to penetrate into them. On the breadth of these molecular pores rests the capacity of solid bodies for condensing[1] on their surfaces considerable quantities of gases and vapours, that is, for depriving them of the mobility proper to their state of aggregation. The gaseous molecules penetrate thereby deeply into the interior of the solid body, so that they are able to pass through the walls of glowing tubes[2] whose briskly moving molecules may often leave wide interspaces, and also, when helped by the force of electrolysis, through platinum foil.[3]

From such observations we are forced to look upon the surfaces of solid bodies, even if most excellently polished, as so rough and uneven that a regular flow immediately over them is scarcely even conceivable. The forward motion of the gas becomes almost entirely annihilated, so that we are justified in looking on the external friction as infinitely great and in putting the slip equal to zero, as was in general done in the older investigations on the friction of gases.

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[1] Or *adsorbing* them, according to the modern nomenclature. Compare the observations of Bunsen and Kayser, *Wied. Ann.* 1883–5.

[2] H. Sainte Claire-Deville and Troost, *Comptes Rendus*, 1863, lvii. p. 965; *Pogg. Ann.* 1864, cxxii. p. 331.

[3] Helmholtz, 'Bericht über Versuche des Herrn Dr. Elihu Root,' *Monatsber. d. Berl. Akad.* 1876, p. 217.

In the limiting conceivable case, in which the mean motion of all the particles of gas close by the wall is zero, we must assume that the velocity of flow which those particles have that are coming towards the wall is entirely taken up by those which are coming from it; each particle, therefore, which meets the wall must not only lose on impact its share of the general velocity of flow, but return with an equal component of velocity in the opposite direction. The loss which it has experienced by the impact would, therefore, in the case considered, amount to *double* the velocity of forward flow.

In reality the loss of velocity will probably be less. I represent it then by $\beta v$, where $v$ denotes the mean velocity of flow and $\beta$ a constant whose value lies between 0 and 2. By the impact of a particle of gas of mass $m$ against the wall, the amount of momentum in the gas is diminished by $\beta m v$. The whole lessening of the momentum in unit time is obtained from this by multiplying it by the number of particles which strike the wall in this time.

In the determination of the pressure by summation of the kinetic energy of all the impacts we found in §§ 11 and 12, by the method first employed by Joule, that the number of particles which strike unit area of the wall in unit time is $\frac{1}{6}NG$, where, as before, $N$ is the number of particles in unit volume and $G$ is a mean value of the speed. We cannot, without further consideration, apply this to the case under consideration, because the method there employed is strictly admissible only for the calculation of the kinetic energy, and not of other magnitudes. This value, therefore, for the number of impinging particles is only approximately correct, and for accuracy we must replace it by the number $\frac{1}{4}N\Omega$ calculated in § 37 and § 41* of the Mathematical Appendices, which differs but inconsiderably from it, and involves instead of $G$ the smaller arithmetical mean $\Omega$ of the molecular speeds.

Multiplication of this number into the loss of momentum of a molecule as found above gives

$$\tfrac{1}{4}\beta mN\Omega v \equiv \varepsilon v$$

for the total loss of momentum experienced per unit area per unit time by a gas which flows along a solid wall with the velocity $v$; or, more shortly expressed, this expression gives the friction of the gas per unit area per unit time on a solid body.

The coefficient which comes into the formula, viz.

$$\varepsilon \equiv \tfrac{1}{4}\beta mN\Omega,$$

is the constant of the external friction of the gas; the formula shows that the theory is in agreement with the law, mentioned already in § 81, which Kundt and Warburg deduced from their observations, viz. that *the external friction is proportional to the density* $\rho \equiv mN$.

For the *coefficient of slip* we have

$$\begin{aligned}\zeta = \eta / \varepsilon &= 0{\cdot}30967\, L / \tfrac{1}{4}\beta,\\ &= 1{\cdot}23868\, L / \beta,\end{aligned}$$

which is therefore simply *proportional to the free path* of the molecules; in denser gases, accordingly, as experiment has proved, the slip on a solid surface is vanishingly small, and it can in general be shown and measured only in rarefied gases.

## 83. Comparison of the Theory with Experiment

The observations of Kundt and Warburg confirm most excellently the law that immediately follows from the foregoing formula, viz. that $\zeta$, just like $L$, is inversely proportional to the density and the pressure of the gas. I forbear citing here in fulness the series of numbers given by them, and limit myself to a setting forth of their conclusions.

From every three or four observations under different pressures made with the same arrangement of apparatus they have deduced a magnitude, denoted by $a$, whose relation to the coefficient of slip is given by

$$aD/\zeta = 2 \times 760,$$

where $D$ denotes the distance in centimetres between the discs of the apparatus employed with Maxwell's method. By means of this formula I have calculated the following values of the coefficient of slip from the numbers given on pp. 544 and 545 of the memoir cited :—

| | $D$ | $a$ | $\zeta$ | $L$ |
|---|---|---|---|---|
| Air | 0·1104 | 0·0149 | 0·0000108 | 0·0000096 |
| | 0·1967 | 0·00700 | 090 | |
| | 0·2802 | 0·00612 | 113 | |
| $H_2$ | 0·1104 | 0·0256 | 0·0000186 | 0·0000178 |
| $CO_2$ | 0·1967 | 0·00505 | 0·00000652 | 0·0000065 |
| | 0·2802 | 0·00351 | 647 | |

In this table all the numbers represent centimetres.

In the last column of the table I have put the values of the free paths already obtained in §§ 78 and 79 from the observations on internal friction, and comparison of these with the values of $\zeta$, in the third column, shows in all these cases that *the coefficient of slip is nearly equal to the free path*, or

$$\zeta = L.$$

From this we obtain for the coefficient $\beta$, which was introduced as in some sort a measure of the roughness of the surface where the friction takes place,

$$\beta = 1{\cdot}23868 \bumpeq 1\tfrac{1}{4}.$$

By means of this assumption, which corresponds with the theoretical requirement $0 < \beta < 2$, complete agreement between theory and experiment is obtained.

Later experiments, undertaken by Warburg[1] to measure the external friction by experiments on transpiration also, confirm this behaviour, but gave smaller values for the coefficient of slip $\zeta$, and therefore larger values for $\beta$. The numbers lately found by Breitenbach,[2] on the contrary, agree very well with those given above.

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[1] *Pogg. Ann.* 1876, clix. p. 399.

[2] *Wied. Ann.* 1899, lxvii. p. 826.

## 84. Phenomena in very Rarefied Gases

The molecular free path increases with increase of rarefaction in the ratio of the increase of the volume; so too, therefore, does the coefficient of slip. But we cannot, therefore, believe that the molecular paths in excessively rarefied gases, as in the vacuum of a mercury air-pump, attain a considerable length. If we assume, for instance, that such a pump were to rarefy the air 100,000 times, or to a pressure of less than $\frac{1}{100}$ mm., the free path, which is 0·00001 cm. under atmospheric pressure, would become 1 cm.; it therefore always remains a remarkably small path for a body projected with a speed of something like 450 metres per second. The number of encounters to which a molecule is exposed remains still very great even in such a condition of rarefaction; it would amount to 46,500 per second.

This calculation certainly does not deserve unconditional confidence, if only because Boyle's law does not hold at such small pressures. But, under any circumstances, this consideration is well suited to show that a gas, even if exceedingly rarefied, is anything but a vacuum. A nominally vacuous space, obtained either by an air-pump or even by Torricelli's method, is distinctly not vacuous, but is so uniformly filled with a medium, of a density certainly very small, that our observations will still give us the impression of the space being continuously filled.

The lengthening of the free path helps, indeed, to remove more quickly and easily any inequalities that exist in the distribution of pressure, temperature, &c. According to the kinetic theory, the transference of any action is the result of the transference of molecules from one layer to another. The longer the paths of the molecules, the wider will therefore be the ranges within which all inequalities will be removed.

This remark remains of force, even when the inequality consists in the distribution of electrical tension. This is the reason why electrical discharges in regions of rarefied air, as, for instance, in Geissler's tubes, take place at far greater distances than in denser air.

The same holds good f [illegible] r [illegible] able phenomenon observed in 1825 by Fresn [illegible] wh [illegible] he was inclined to interpret as a repulsion betw [illegible] heate [illegible] bodies. The essentially similar actions which Crookes[2] observed during weighings in rarefied spaces, as well as the motions observed in the apparatus[3] invented by him, and called the *radiometer* or *light-mill*, are to be explained by the same ideas.

The vanes of the little mill, which are black on one side and white on the other, are warmed by radiated heat, or even by light—since a luminous ray is only a heat-ray which is also luminous to the eye—but they are warmed unequally, and the black side the more strongly. If, therefore, a particle of air impinges on a black face it carries off more heat, *i.e.* flies off with greater speed, than if the collision had been against a white face. The reaction which it exerts on the vane in its rebound is, therefore, greater when it leaves the warmer black face than at the colder white side. Consequently, the mill must so turn that the white side of the vanes precedes.

If we think of the immense speed with which the gaseous molecules move, it seems scarcely necessary to specially prove that the force that results from this unequal heating is really sufficient to bring about this action. But since the proof can be easily given independently of the hypotheses on which the theory of gases rests, we will calculate the magnitude of the energy for a simple case, so chosen that the necessary experimental data are known. Suppose the vanes to be made of aluminium foil of 1 sq. cm. area, and to be blackened with soot on one side, and suppose the heating to be caused, not by a source outside the instrument, but by the glass envelope itself, which we will take to be 1 degree C. warmer than the mill.

Lehnebach[4] has observed that glass and sooted surfaces radiate with equal intensity towards a region of rarefied

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[1] *Ann. Chim. Phys.* 1825 [2] xxix. p. 57; *Œuvres Complètes*, 1868, ii. p. 667.

[2] *Phil. Trans.* 1873, clxiii. p. 277.

[3] *Quarterly Journal of Science*, 1875, xii. p. 337.

[4] *Pogg. Ann.* 1874, cli. p. 96.

air; according to Kirchhoff's[1] law concerning the emission and absorption of radiant heat, they have therefore equal coefficients of absorption also. Hence the conclusion that the radiation received by the blackened side of the vane from the glass envelope is equal to that which the blackened side of the vane would send out to the glass wall if it were as much the warmer as the glass envelope is.

I have calculated[2] in absolute measure the amount of heat which a warmed black surface radiates to the receiver of an air-pump under which it is placed from the observations made by Stewart and Tait,[3] on the heating of a blackened disc of aluminium in a vacuum of 7·6 mm. pressure. I have found the value

$$h = 0{\cdot}0017$$

for the constant of radiation, referred to a millimetre, second, and degree C. as units; with centimetres substituted for millimetres, we have

$$h = 0{\cdot}00017,$$

and this number simply means that the heat radiated in one second by a square centimetre of a blackened surface of aluminium at a temperature 1 degree C. above its environment would suffice to raise 0·00017 gram of water through 1 degree C.—that is, is equal to 0·00017 calorie. From observations by Dulong and Petit, and also by F. Neumann, I found $h = 0{\cdot}00013$. Later on Lehnebach found a value which, reduced to 1 degree C., is $h = 0{\cdot}00015$; and, lastly, Kundt and Warburg[4] have obtained $h = 0{\cdot}00014$ in the same units. The perfect agreement between these numbers vouches for their correctness.

A vane of the radiometer of 1 sq. cm. area would, therefore, receive on its blackened side a radiation of about 0·00015 calorie in a second if the glass envelope were the warmer by 1 degree. According to Stewart and Tait's observations, the emissivity of a surface of bare aluminium is four times smaller, so that, in accordance with Kirchhoff's law, it seems just to assume that a vane made of aluminium will absorb in the same time only a fourth part of that amount of heat, *i.e.* about 0·00004 calorie. The difference between the two amounts of heat received, viz. 0·00011 calorie, which is the energy that drives the radiometer, is capable of raising 0·00011 × 425 = 0·05 gram by 1 metre, or 5 grams by 1 cm. [that is, the power is 5 gm. cm. per sec.]. This energy, acting on a vane, would certainly be capable of turning the light-mill round, and, indeed, even if the difference in temperature of the vanes and envelope were 100 or 1,000 times smaller than 1 degree. For with the mill there moves only the rarefied, and therefore light, air which has to overcome at the wall only an external friction, which is very much diminished by the rarefaction.

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[1] *Pogg. Ann.* 1860, cix. p. 275; *Untersuchungen über das Sonnenspectrum*, 2nd ed. Berlin 1862, p. 22.

[2] *Ibid.* 1868, cxxxv. p. 285.

[3] *Proc. Roy. Soc.* 1865, xiv. p. 339; *Phil. Mag.* 1865 [4] xxx. p. 314.

[4] *Pogg. Ann.* 1875, clvi. p. 208.

## 85. Influence of the Temperature on the Viscosity

Since according to the kinetic theory the friction of gases is to be looked upon as a consequence of the molecular motion, the coefficient of friction must be variable with the temperature if that theory is true; and we may expect, from the reasons given in § 76, that it increases with rise of temperature. Every observer who has investigated the influence of the temperature on the friction has found this expectation justified. Only in respect of the *rate* of the increase with the temperature have the results of different observers shown differences which were at first hard to explain.

We can only conclude,[1] from the observations of Graham[2] on the flow of gases through tubes, that the friction of gases really increases with the temperature, as the theory requires; we might draw the further conclusion from them that the increase of friction with the temperature is in nearly the same ratio for all gases. Both speak in favour of the theory; for the speed of the molecules, which comes as a factor into the formula for the coefficient of viscosity, increases with the temperature at nearly the same rate for all gases; and it is not unreasonable to expect the same also with respect to the free path.

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[1] *Pogg. Ann.* 1866, cxxvii. p. 369.

[2] *Phil. Trans.* 1846 and 1849.

As a fact, the earlier of the more accurate measures made on the increase of the coefficient of viscosity with the temperature seemed to result in a simple relation to the coefficient of expansion, and therefore to a magnitude which has nearly the same value for all gases. Maxwell[1] first drew from his observations that the coefficient of viscosity of air increases in the same ratio as the absolute temperature, and thus proportionally to

$$1 + a\vartheta,$$

where $\vartheta$ is the temperature measured from freezing-point, and $a$ is the coefficient of expansion. It was, indeed, proved by the later experiments of other observers[2] that the viscosity, at least of atmospheric air, does not increase with the temperature so rapidly as Maxwell had believed; but it was conclusively shown that it rises more rapidly than the square root of the absolute temperature, *i.e.* faster than the magnitude

$$\sqrt{(1 + a\vartheta)}.$$

There can therefore be no further doubt that, in the formula for the coefficient of viscosity (§ 78)

$$\eta = 0{\cdot}30967\ \rho L \Omega,$$

not only does the speed $\Omega$, which is proportional to that square root, increase with the temperature, but so also does the free path $L$.

The endeavour was then made at first to express the dependence of the coefficient of viscosity on the temperature by a factor of the form

$$(1 + a\vartheta)^n,$$

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[1] *Phil. Trans.* 1866, clvi. p. 249; *Scientific Papers*, ii. p. 1.

[2] O. E. Meyer, *Pogg. Ann.* 1873, cxlviii. p. 203. Puluj, *Wiener Sitzungsber.* Abth. 2, 1874, lxix. p. 287; lxx. p. 243; 1876, lxxiii. p. 589. von Obermayer, *ibid.* Abth. 2, 1875, lxxi. p. 281; 1876, lxxiii. p. 433; *Carl's Repert.* 1876, xii. p. 13; 1877, xiii. p. 130. Warburg, *Pogg. Ann.* 1876, clix. p. 403.

d this formula seemed to suit the case of atmospheric when $n$ was taken equal to $\frac{3}{4}$. Since the molecular speed ers with the temperature proportionally to $\sqrt{(1 + a\vartheta)}$, molecular free path must then be proportional to

$$(1 + a\vartheta)^{\frac{1}{4}}.$$

According to the observations of C. Barus[1], who investigated the flow through capillary tubes within a very le range of temperature, $n = \frac{2}{3}$ both for air and for drogen; with this value the formula holds from 0° to 00°. For both gases, therefore, the free path would increase proportionally to

$$(1 + a\vartheta)^{\frac{1}{6}}.$$

Experiments with other gases showed, on the contrary, t this value for $n$ cannot hold in general. Puluj[2] ained by the oscillation method the value $n = 0{\cdot}92$ for omic acid, and von Obermayer[3] observed with capillary tubes values for $NO_2$, $CO_2$, ethylene and ethyl chloride, ich were all nearly equal to 1. Eilhard Wiedemann[4] nd for these gases that the value for $n$ is variable with temperature, and is the smaller the higher the temperature. S. W. Holman[5] arrived at the same result, and therefore expressed his results by the usual series of wers.

O. Schumann[6] chose a formula with a double factor the form

$$(1 + \gamma\vartheta)^2 \sqrt{(1 + a\vartheta)}$$

represent his observations; the square root here expresses dependence of the molecular speed $\Omega$ on the temperature, while the quadratic factor is to express the change of the second quantity occurring in the formula for the coefficient of viscosity, viz. the molecular free path. The second power is here chosen, because from the formula

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[1] *Bull. of the U. S. Geological Survey, No.* 54, Washington 1889; *Amer. rn. of Science*, 1888 [3] xxxv. p. 407; *Wied. Ann.* 1889, xxxvi. p. 358.

[2] *Wiener Sitzungsber.* 1876, lxxiii. Abth. 2, p. 589.

[3] *Wiener akad. Sitzungsanzeiger*, 1876, No. 8; *Carl's Repert.* 1876, xii. 5.

[4] *Arch. d. Sc. Phys. et Nat.* 1876, lvi. p. 273. Breitenbach, *Wied. Ann.* lxvii. p. 816.

[5] *Proc. Amer. Acad. Boston.* 1877, xii. p. 41; 1885, xxi. p. 1; *Phil. Mag.* [5] 81; xxi. p. 199.

[6] 'Ueber die Reibung von Gasen u. Dämpfen u.s.w.' *Tübinger Habilita- schrift*; *Wied. Ann.* 1884, xxiii. p. 353.

$$L = \lambda^3/\pi s^2\sqrt{2}$$

we may assume that the free path can depend on the temperature only in so far as the central section of the sphere of action is variable; hence $\gamma$ might be looked on as the measure of the diminution which $s$ the radius of the sphere of action undergoes with rise of temperature. The new formula excellently satisfies the observations which Schumann made by Maxwell's oscillation method, yet it seems to correspond less well to the transpiration experiments which Barus[1] has carried out within a far larger range of temperature.

The reasons for the assumption that the section of the sphere of action diminishes as the temperature rises have been given already in § 71. These depend for the most part on conceptions which would be as well fitted to explain the deviations from the laws of perfect gases, so that they might be applied to vapours. But in the question of actual gases, those attempts at explanation will certainly meet with most acceptance which do not assume a real diminution of the molecules or their spheres of action, but only an apparent alteration. From this point of view Sutherland's view deserves to be preferred to all others. According to him we have not to deal with the real sphere of action, but with an apparent sphere of action which is larger than the real one.

The attractive forces which are recognised by us in liquids and solids as cohesion and hardness are, according to Joule and Lord Kelvin's experiments, not absent from the molecules of gases too. Certainly they only come into play when two molecules come very closely together; but they may then cause two molecules to collide which without such attraction would have passed by each other.

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[1] *Bull. U. S. Geological Surv. No.* 54, p. 278; *Wied. Ann.* 1889, xxxvi. p. 386.

The forces of cohesion have therefore the same result as an increase of the section of the sphere, which with Clausius we have called the sphere of action, would have. The amount of this enlargement depends on the speed with which the particles move, and, therefore, on the temperature of the gas; it is the greater the less the speed or the lower the temperature. The sphere of action will therefore appear to be less enlarged at higher temperatures than at lower, and this produces the same result as if it becomes smaller when the temperature rises. The consequence of this behaviour is an increase of the molecular free path with the temperature.

We might *a priori* take it as very probable that this view is right, because the gases for which tolerably large or, indeed, variable values of $n$ have been found belong to those which have strong cohesion, and can therefore be condensed to liquids with proportionate ease.

In bringing forward this hypothesis to explain the phenomena Sutherland[1] had really the greatest success. According to his theory, explained in § 71, the free path $L$ at the absolute temperature $\Theta$ is connected with its value $L_0$ at the freezing-point by the relation

$$L = L_0(1 + aC)/(1 + C/\Theta).$$

In the constant magnitude $C$ which here occurs we have to see a measure of the strength of the attractive forces which act between the gaseous molecules, and, therefore, a measure of the cohesion of the gaseous medium; $a$ is the coefficient of expansion. If we introduce this value of $L$ and also the value

$$\Omega = \Omega_0\sqrt{(1 + a\vartheta)}$$

into the formula for the coefficient of viscosity

$$\eta = 0{\cdot}30967\, \rho L \Omega,$$

we obtain the equation

$$\eta = \eta_0 \frac{1 + aC}{1 + C/\Theta}\sqrt{(1 + a\vartheta)},$$

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[1] *Phil. Mag.* 1893 [5] xxxvi. p. 507.

which expresses the value of $\eta$ at the temperature $\Theta \equiv \vartheta + a^{-1}$ in terms of $\eta_0$ which corresponds to the freezing-point.

With this formula Sutherland first succeeded in very exactly reproducing the law of the observations which Holman had made on the viscosity of atmospheric air at different temperatures. Putting $C = 113$, he calculated the following values of the ratio $\eta/\eta_0$ which are put opposite the corresponding observed values:[1]

*Atmospheric Air.*

| $\vartheta$ | $\eta/\eta_0$ | |
|---|---|---|
| | Observed | Calculated |
| 14 | 1·038 | 1·040 |
| 43 | 1·118 | 1·120 |
| 67·8 | 1·185 | 1·186 |
| 88·8 | 1·241 | 1·241 |
| 99·2 | 1·270 | 1·267 |
| 124·4 | 1·331 | 1·329 |

With the same value of $C$ he was able to represent right satisfactorily the ratios observed by Barus.[2]

*Atmospheric Air.*

| $\vartheta$ | $\eta/\eta_0$ | |
|---|---|---|
| | Observed | Calculated |
| 442 | 1·991 | 1·976 |
| 565 | 2·083 | 2·183 |
| 569 | 2·149 | 2·190 |
| 592 | 2·117 | 2·225 |
| 982 | 2·711 | 2·781 |
| 995 | 2·693 | 2·799 |
| 1210 | 3·214 | 3·179 |
| 1216 | 3·147 | 3·185 |

There is a still better agreement between the formula and Holman's[3] observations on the viscosity of carbonic acid, if for this gas the larger value $C = 277$ is put.

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[1] *Proc. Amer. Acad.* 1885, xxi. p. 13.

[2] *Amer. Journ. of Sci.* 1888 [3] xxxv. p. 408.

[3] *Proc. Amer. Acad.* 1885, xxi. p. 16.

*Carbonic Acid.*

| $\vartheta$ | $\eta/\eta_0$ | |
|---|---|---|
| | Observed | Calculated |
| 18 | 1·068 | 1·066 |
| 41 | 1·146 | 1·148 |
| 59 | 1·213 | 1·211 |
| 79·5 | 1·285 | 1·280 |
| 100·2 | 1·351 | 1·351 |
| 119·4 | 1·415 | 1·414 |
| 142 | 1·484 | 1·490 |
| 158 | 1·537 | 1·541 |
| 181 | 1·619 | 1·614 |
| 224 | 1·747 | 1·746 |

After this excellent agreement between observation and calculation, we can scarcely doubt the correctness of the explanation given by Sutherland. We may therefore find room here also for the values of the constant of cohesion which Sutherland has deduced from von Obermayer's[1] observations.

$N_2$ Nitrogen . . . $C = 84$
$O_2$ Oxygen . . . $= 127$
CO Carbon monoxide . $= 100$
$N_2O$ Nitrous oxide . . $= 260$
$C_2H_4$ Ethylene . . . $= 272$

## 86. Viscosity of Vapours

Of the observations hitherto carried out many refer to gases which would more properly be termed vapours, since they can be changed into liquids by a simple increment of pressure. To this category belongs even that gas, the viscosity of which has been investigated by many observers with especial care, viz. carbonic acid.

This example is quite sufficient to prove the right of those substances to be denoted as gases. But the true basis of this right lies in the fact that the vapours have been examined as to their viscosity in circumstances under which they satisfy the laws of perfect gases with sufficient exactness. For it may be concluded, from Boyle's law holding, that the assumptions on which the gaseous theory rests are right; and if this is the case, the chief law of gaseous friction must also hold, viz. that the coefficient of viscosity is independent of the pressure.

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[1] *Wiener Sitzungsber.* 1876, lxxiii. Abth. 2, p. 433; *Carl's Repert.* 1877, xiii. p. 130.

Further experiments on the friction of vapours have been made by Puluj[1] and Schumann[2] by the oscillation method; numerous experiments also on the transpiration of vapours have been carried out by Lothar Meyer,[3] partly by himself and partly in co-operation with Schumann and Steudel. The law of the non-dependence of the coefficients of viscosity and transpiration on the pressure of the vapour was proved, by the measurements of these coefficients, for the cases when the conditions of the experiments were so chosen that the vapour was sufficiently far from its point of condensation. The temperature, therefore, must be so high and the pressure so low that the vapour can follow the laws of perfect gases, and, therefore, can exhibit the normal density, at least approximately.

The values of the coefficient of viscosity measured under such circumstances stand in a simple relation to the chemical nature of the substances. Substances of similar constitution have equal, or at least approximately equal, coefficients of viscosity. Thus the following values of the coefficient of viscosity were found always with tolerable exactness for the different kinds of compounds, whatever value $n$ might have in the formulæ, provided only that it exceeds 1:

| | | |
|---|---|---|
| Alcohols . . | $C_nH_{2n+2}O$ | $\eta = 0{\cdot}000142$ |
| Chlorides . . | $C_nH_{2n+1}Cl$ | 150 |
| Esters . . . | $C_nH_{2n}O_2$ | 155 |
| Bromides . . | $C_nH_{2n+1}Br$ | 182 |
| Iodides . . . | $C_nH_{2n+1}I$ | 210 |

Against the correctness of these numbers we may remark, as Lothar Meyer did himself, that they do not agree with the observations of Graham for methyl chloride and ethyl chloride which are cited in § 79. I believe, however, that we must not see in this any ground for doubt; for Graham's measures were made at quite a different temperature from those of the observers at Tübingen. On the contrary I should sooner think that Graham's observations are of small value because they were made with a short tube, the section of which was neither circular nor regular.[1] If, however, Lothar Meyer's observations also were to be affected by a constant error, that would be without effect on the mutual agreement of the numbers; and the conclusion remains that the entrance of chlorine or bromine or iodine into a chemical combination substantially increases the viscosity of the vapour.

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[1] *Wiener Sitzungsber.* 1878, lxxviii. Abth. 2, p. 279; *Carl's Repert.* 1878, xiv. p. 573.

[2] *Wied. Ann.* 1884, xxiii. p. 353.

[3] *Ibid.* 1879, vii. p. 497; 1881, xiii. p. 1; 1882, xvi. pp. 369, 394.

Within each group, however, the value of the viscosity is the same for all substances. In this lies a confirmation of the proposition stated in § 79, that the viscosity-coefficients of gases whose molecules are made up of a considerable number of atoms are of nearly the same magnitude. They are certainly not so different from each other as the coefficients of viscosity of bodies in which fewer atoms are bound together to form the molecule; this is seen also from a comparison of the numbers just given, both with each other and with other numbers tabulated earlier.

If, as this shows, vapours obey the laws of viscosity in many respects like gases, there still remain essential differences to take into account, and these we have now to consider more in detail.

## 87. Dependence on the Temperature

The first of these differences concerns the mode in which the viscosity of vapours depends on the temperature. Vapours exhibit a much more marked variation with temperature than gases. Hence Sutherland's formula, which is in excellent agreement with the behaviour of gases, is only imperfectly satisfied by many vapours.

We can at once see that the validity of the formula may be limited; for it is not possible by a determination of the value of $C$ to represent every possible ratio in which the viscosity may increase with the temperature.

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[1] Capillary tube *K*, *Phil. Trans.* 1849, pp. 353, 357.

This constant $C$ serves as a measure of the cohesion of the molecules of the vapour in comparison with the energy of their motion. With vapours we must expect that $C$ will assume a larger value, which is to be taken the larger the more easily the vapour can be condensed to the liquid state. Considering then that $C$ increases, the factor

$$1/(1 + C/\Theta) \equiv \Theta/(C + \Theta),$$

which comes into the formula, takes approximately the simpler form

$$\Theta/C,$$

and is thus simply proportional to the absolute temperature $\Theta$ when $C$ is so large that the value of $\Theta$ is small compared with it. The length of the free path in such vapours will thus increase in nearly the same ratio as the absolute temperature, or will be proportional to

$$1 + a\vartheta$$

This limiting case cannot, however, be exceeded, so that on this theory, as has been already indicated in § 71, the free path can only increase as rapidly as $1 + a\vartheta$ at the most when the temperature rises. The coefficient of viscosity, which, in accordance with the formula

$$\eta = 0{\cdot}30967\ \rho\Omega L,$$

contains, in addition to $L$, the second factor $\Omega$ that is variable with the temperature, cannot therefore, from Sutherland's formula, increase with the temperature more rapidly than in proportion to

$$(1 + a\vartheta)^{\frac{3}{2}}.$$

But Synesius Koch[1] has shown by experiments which embrace a range of more than 100 degrees of temperature that the viscosity of mercury vapour increases with the temperature proportionally to

$$(1 + a\vartheta)^{1},$$

in which the coefficient of expansion $a$ is taken equal to

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[1] *Wied. Ann.* 1883, xix. p. 857.

0·003665, as for gases. Mercury vapour therefore alters its viscosity in a rather larger ratio than can be explained by Sutherland's theory.[1]

We meet with similar difficulties in regard to the observations made by O. Schumann[2] on the viscosity of the vapour of benzol and of different esters; for the function of the temperature that represents the behaviour of benzol is

$$(1 + 0{\cdot}00185\,\vartheta)^2\sqrt{(1 + 0{\cdot}004\,\vartheta)},$$

in which each term increases more rapidly with the temperature than the theory can explain. For many of the esters, certainly, the law of alteration with temperature that was found lies between the theoretical limits; but the function

$$(1 + 0{\cdot}00164\,\vartheta)^2\sqrt{(1 + 0{\cdot}004\,\vartheta)},$$

which Schumann has deduced as the most probable mean of all his observations on esters, increases nearly as rapidly as the extreme limiting case admissible under Sutherland's theory.

Let us now examine whether Schumann's observations satisfy this limiting value, and for this let us express the coefficient of viscosity by

$$\eta = \eta_0(1 + a\vartheta)^{\frac{3}{2}},$$

where $\eta_0$ is its value at 0° C., and $a$ is taken for all vapours equal to 0·00367; or more simply let us put

$$\eta = H\Theta^{\frac{3}{2}},$$

where $H$ is a constant and $\Theta$ the absolute temperature; we then find a tolerably good agreement between the theoretical formula and the results of experiment. The following tables contain the mean values of the magnitudes measured by Schumann and the values of $H$ calculated from them.

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[1] Compare § 92.

[2] O. Schumann, *Tübinger Habilitationsschrift*, 1884; *Wied. Ann.* 1884, xxiii. p. 353.

| | $\vartheta$ | $\Theta$ | $10^6\eta$ | $10^{10}H$ |
|---|---|---|---|---|
| Benzol . . . . . . | 19·0<br>70·1<br>100 | 291·5<br>342·6<br>372·5 | 77·23<br>98·42<br>114·8 | 155·2<br>155·2<br>159·7 |
| Methylformate . . . | 20<br>100 | 292·5<br>372·5 | 92·28<br>135·2 | 184·5<br>184·1 |
| Propylacetate . . . | 15·0<br>77·8<br>100 | 287·5<br>350·3<br>372·5 | 74·29<br>95·39<br>109·6 | 152·4<br>145·5<br>152·4 |
| Methylisobutyrate . . | 24·0<br>65·5<br>100 | 296·5<br>338·0<br>372·5 | 75·36<br>99·86<br>112·2 | 147·6<br>165·6<br>156·1 |
| Ethylpropionate . . . | 16·1<br>68·6<br>99·9 | 288·6<br>341·1<br>372·4 | 74·99<br>105·4<br>116·1 | 153·0<br>167·3<br>161·6 |
| Isobutylformate . . . | 17·7<br>63·6<br>99·9 | 290·2<br>336·1<br>372·4 | 83·01<br>97·21<br>114·2 | 167·9<br>157·8<br>158·9 |
| Isobutylacetate . . . | 16·1<br>100 | 288·6<br>372·5 | 76·40<br>112·0 | 155·8<br>155·8 |

From the mean values of these numbers found for $H$ I have calculated the value of the coefficient of viscosity $\eta_0$ at 0°, and thence the values of $\eta$ at the temperatures of the experiments in order to see if the formula

$$\eta = \eta_0(1 + a\vartheta)^{\frac{3}{4}},$$

with the value of $a$, viz. 0·00367, which is satisfied by gases, reproduces the observed values of the viscosity within the limits of possible errors of observation. I have thus obtained the following values of $10^6\eta$ for the vapour of benzol, which I have tabulated along with those observed by Schumann and those also which are calculated by his formula.

*$10^6\eta$ for Benzol Vapour.*

| $\vartheta$ | Meyer's calculation | Schumann's observation | Schumann's formula |
|---|---|---|---|
| 0 | 70·48 | | 68·94 |
| 19·0 | 77·98 | 77·23 | 76·56 |
| 70·1 | 99·36 | 98·42 | 99·51 |
| 100 | 112·65 | 114·8 | 114·6 |

The new formula therefore agrees with the observations not essentially worse than Schumann's, which contains a disposable constant. For the esters investigated by Schumann I have likewise calculated the following values, which I tabulate opposite the observed values :—

*Values of* $10^6\eta$.

| | $\vartheta$ | Meyer's calculation | Schumann's observation |
|---|---|---|---|
| Methylformate . . . | 0 | 83·78 | |
| | 20 | 93·18 | 92·28 |
| | 100 | 133·9 | 135·2 |
| Propylacetate . . . | 0 | 70·70 | |
| | 15 | 73·18 | 74·29 |
| | 77·8 | 98·41 | 95·39 |
| | 100 | 107·9 | 109·6 |
| Methylisobutyrate . . | 0 | 70·36 | |
| | 24 | 79·86 | 75·36 |
| | 65·5 | 94·32 | 99·86 |
| | 100 | 112·5 | 112·2 |
| Ethylpropionate . . . | 0 | 72·24 | |
| | 16·1 | 78·74 | 74·99 |
| | 68·6 | 101·2 | 105·4 |
| | 99·9 | 115·4 | 116·1 |
| Isobutylformate . . . | 0 | 72·65 | |
| | 17·7 | 79·86 | 83·01 |
| | 63·6 | 99·53 | 97·21 |
| | 99·9 | 116·1 | 114·2 |
| Isobutylacetate . . . | 0 | 70·08 | |
| | 16·1 | 76·39 | 76·40 |
| | 100 | 112·0 | 112·0 |

The calculated numbers fit in well as a rule with the course of those observed. We may therefore assert with certainty that Sutherland's theory corresponds pretty exactly to reality even in the limiting case now considered, in which the cohesive forces of the vapour are taken extremely large. The deviations of the theoretical formula from the results of observation are always only a few hundredths of the magnitudes measured. We might therefore defend the view that the differences may be due only to errors of observation, arising partly in the measurement of the viscosity and partly in the estimation of the temperature. But against this view there is the circumstance that a fluctuation is shown in the values of the constant $H$ first calculated which occurs in several esters in almost exactly similar fashion.

We are also forced to the opinion that these fluctuations are not entirely fortuitous by the consideration that the theory is not without other underlying causes, which may be adduced, along with that theoretically investigated by Sutherland and justified by observation, in order to explain the large variation of viscosity in vapours with the temperature.

## 88. Dissociation

Among the causes which make vapours deviate from the laws of perfect gases the most important depends upon the dissociation which the molecules undergo as well from rise of temperature as from diminution of pressure.

In earlier sections of this book we have several times spoken of this dissociation. Especially in §§ 48–51 has its nature been described and the influence which it exerts on the density of a vapour. In a vapour the molecules are not all of the same size and mass as in a perfect gas. The case often occurs, in consequence of the forces of cohesion, in which two molecules which chance to come near enough to each other join together to form one molecule of double size; and just as frequently the case arises that such a double molecule splits up again into its constituents, either as a result of collision with another molecule, or simply in consequence of an increase of speed, which not only breaks up the whole molecule, but also partly tears apart the atoms bound up in it. Hence it happens that a vapour is always a mixture of large and small molecules.

The ratio in which the simple and compound molecules are mixed together differs with the temperature; for an increase of speed, as brought about by a rise of temperature, increases the probability of the division of the larger masses. The number of simple molecules therefore increases when the temperature rises, and that of the compound molecules when the temperature falls, until finally, at a definite temperature, all are broken up and the perfectly gaseous state is attained. At lower temperatures, on the contrary, the number of the compound molecules is in excess.

This behaviour of the molecules explains, as before remarked, the fact that the density of vapours, when compared with the density of air or of any other gas under the same pressure but at different temperatures, does not remain constant. Since, in accordance with Avogadro's law, the number of molecules in unit volume is the same for all gases at the same pressure and temperature, we find a smaller value of the vapour-density if the molecules are broken up into smaller ones at higher temperatures; at lower temperatures, on the contrary, when all the molecules are joined together, either in pairs or larger aggregates, the vapour-density will turn out much larger.

A change of pressure has just the same kind of effect upon the degree of dissociation attained. If the pressure is diminished by an enlargement of the volume, the molecules separate from each other in greater number because they acquire greater freedom of movement, and are less exposed to the forces of cohesion. But an increment of pressure brings the particles nearer together, and affords them more frequent opportunity of combining.

If these views are right, the law of alteration of the density of a vapour with its pressure and temperature must be determinable from theoretical considerations that go more deeply into the nature of the phenomena. The first who succeeded in finding this law was J. W. Gibbs.[1] In addition to the general laws of gases he employed the two principal laws of Thermodynamics, viz. the theorem of energy and the theorem of entropy; from these he deduced formulæ that agree excellently with experiment. Van der

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[1] *Trans. Connecticut Acad.* New Haven 1876, iii. pt. 1, p. 234. Under the title of 'Thermodynamical Studies, 1892,' published in German by Ostwald, p. 204. Report on this memoir by Maxwell in *Proc. Camb. Phil. Soc.* ii.; *Amer. Journ. Sci.* [3] xiii. p. 380; *Scientific Papers*, ii. p. 498.

Waals[1] treated this problem similarly, and later, in a somewhat different way, which starts with the conception of atoms as vortex rings (§ 124), J. J. Thomson[2] discussed it by an investigation of the probable mean intervals during which a pair of molecules remain separate or combined. Almost simultaneously Boltzmann[3] proved the theoretical formula by a method which depends entirely on the conceptions of the kinetic theory of gases. He investigated the probability of the different possible results of an encounter, and thus determined how often, on an average, two particles on meeting join together, and how often on an average two particles joined together separate on a collision; from this we obtain the number of separate molecules and that of combined pairs of molecules, and these numbers give finally the density of the vapour. L. Natanson[4] proceeded similarly, and also G. Jäger,[5] who considerably simplified the formula by introducing approximate values.

I must omit from this book a reproduction of these theories and formulæ; we have only to investigate whether the dissociation has any effect on the value of the coefficient of viscosity, and, if so, of what kind this effect will be.

## 89. Alteration of Viscosity by Dissociation

We can scarcely doubt that a breaking up of the molecules must be of importance for the viscosity in a vapour as it is for its density. But whether the viscosity is increased or diminished by the dissociation is a question not so surely and generally answered as that of the influence of dissociation on the vapour-density. For the factors which form the mathematical expression for the coefficient of viscosity change their values in opposite directions when the molecules are broken up. The free path will certainly become no smaller, but in all probability larger, because the section of the molecular sphere of action cannot be increased, but only diminished, by the separation of the molecules; and of the other two factors the density $\rho$ decreases and the speed $\Omega$ increases as the dissociation progresses, but their product $\rho\Omega$ decreases, since the magnitude $\rho\Omega^2$ remains constant while the pressure is unaltered. Hence the formula for the coefficient of friction $\eta$ contains two factors, of which the one, $L$, is probably greater when separation occurs, and the other, $\rho\Omega$, smaller. Consequently without closer consideration or numerical calculation we cannot say how $\eta$ will be altered.

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[1] *Versl. en Mededeel. d. K. Ak. v. Wet. Amst.* 1880 [2] xv. p. 199.

[2] *Phil. Mag.* 1884 [5] xviii. p. 233.

[3] *Wien. Sitzungsber.* 1883, lxxxviii. Abth. 2, p. 861; *Wied. Ann.* 1884, xxii. p. 39.

[4] *Wied. Ann.* 1889, xxxviii. p. 288.

[5] *Wien. Sitzungsber.* Abth. 2, 1891, c. p. 1189; 1895, cii. p. 671; Winkelmann's *Handbuch der Physik*, 1896, ii. pt. 2, p. 561.

We find, however, a surer way of answering this question by looking on the partially dissociated vapour as a mixture of two different gases, of one gas, that is, which consists of the dissociated simple molecules, and of another whose molecules are unbroken-up and are consequently of, say, doubled size. If we then employ the formulæ developed in § 80 for the viscosity of a mixture we must put in them

$$m_2/m_1 = 2,$$

if we limit ourselves to the simplest case, in which only double molecules occur, and not triple, quadruple, &c.

We employ the formula for the coefficient of viscosity of the partially dissociated vapour in the form

$$\eta = \eta_1 \frac{(N_1/N + 2N_2/N)^{\frac{1}{2}}}{\{N_1/N + 2^{\frac{3}{4}}(\eta_1/\eta_2)^{\frac{3}{2}}(N_2/N)\}^{\frac{2}{3}}},$$

but avoid replacing the magnitudes $N$, which denote the numbers of the different molecules, by the values of the whole and partial pressures, since Boyle's law does not hold. But instead of the numbers $N$ we may put the values of the density which the vapour has when partially and completely dissociated. From the formula for the mean molecular weight

$$m = (N_1 m_1 + N_2 m_2)/N = m_1(N_1 + 2N_2)/N$$

we obtain

$$\delta = D(N_1 + 2N_2)/N$$

on multiplying by $N$, the whole number of the particles, and putting

$$\delta \equiv Nm, \quad D \equiv Nm_1,$$

so that $\delta$ represents the density of the vapour in its actual state in which it is partly dissociated, and $D$ the density which it would attain when all the molecules were broken up and the vapour therefore completely dissociated. Since, further, $N_1 + N_2 = N$, we may express $N_1$ and $N_2$ by the densities $\delta$ and $D$; for the foregoing formulæ give

$$N_1/N = (2D - \delta)/D, \quad N_2/N = (\delta - D)/D.$$

Hence it follows that the coefficient of viscosity $\eta$ of the partially dissociated vapour is represented by

$$\eta = \eta_1 \delta^{\frac{1}{2}} D^{\frac{1}{6}} \{2D - \delta + 2^{\frac{3}{4}}(\eta_1/\eta_2)^{\frac{3}{2}}(\delta - D)\}^{-\frac{2}{3}},$$

in which $\eta_1$ is the coefficient of viscosity of the vapour when completely dissociated into simple molecules; $\eta_2$, on the contrary, denotes the value of the coefficient of viscosity for this substance if no dissociation at all has taken place, but all the molecules are combined together in pairs. There further come into the formula the magnitudes $\delta$ and $D$, which represent respectively the density of the actual vapour and the value which the density would attain at the same pressure and temperature if *all* the molecules were dissociated into simple molecules by dissociation. The coefficient of viscosity therefore of a vapour appears to be variable with its density, in contradistinction to the behaviour of perfect gases.

It follows that the formula is not to be used for such vapours as exhibit no dependence of their viscosity on the pressure; and we may conclude that in all cases in which the coefficient of friction has been found to be independent of the pressure the dissociation of the molecules has been of no material influence. This occurs in most of the vapours hitherto experimented on; especially is it shown in the experiments of Puluj[1] on the friction of ether vapour, and in those of Schumann[1] on benzol and the esters—in most of his experiments at least. Schumann, however, mentions that with methyl formate a slight increase of the coefficient of friction, amounting to about 1 per cent., was noted when the pressure at 21·8° was raised from 37·47 to 46·37 cm. of mercury, or nearly to the pressure 50·1 cm. corresponding to the point of saturation. Perhaps in this small variability we may see a confirmation of our theoretical formula.

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[1] *Wiener Sitzungsber.* 1878, lxxviii. Abth. 2, p. 279.

For a sure resolution of the question whether the formula correctly represents the actual behaviour of vapours we may, with a better prospect of success, employ in our calculations the observations, already mentioned in § 77, which Warburg and von Babo[2] have made on the friction of carbonic acid under high pressures. For these experiments confirm the theoretical formula in that they both agree in showing that the viscosity depends on the pressure only in so far as it varies with the density.[3] Probably, too, the observations of Houdaille[4] on the variability of the viscosity of water-vapour may help to good results.

## 90. Comparison of the Theory with the Behaviour of Carbonic Acid

In order to submit the numerical results of the observations to the theoretical calculation I have put the formula for the coefficient of viscosity $\eta$ in the simpler form

$$\eta = B\delta^{\frac{1}{2}}(A - \delta)^{-\frac{2}{3}}$$

by making the following substitutions, for the sake of shortness, in the magnitudes that are independent of the density $\delta$, viz.:

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[1] *Wied. Ann.* 1884, xxiii. p. 394.

[2] *Ber. üb. d. Verh. d. naturf. Ges. zu Freiburg i. B.* 1882, viii.; *Wied. Ann.* 1882, xvii. p. 390; abstract in *Berl. Sitzungsber.* 1882, p. 509.

[3] Warburg and von Babo, *Results*, § 12, i. 3. Hence the viscosity seems to be connected with the density much more simply than with the pressure.

[4] *Fortschr. d. Phys.* 1896, 52. Jahrg. I. p. 442.

$$\varepsilon \equiv 2^{\frac{3}{4}}(\eta_1/\eta_2)^{\frac{3}{2}}, \quad A \equiv D(2-\varepsilon)/(1-\varepsilon), \quad B \equiv \eta_1 D^{\frac{1}{6}}(1-\varepsilon)^{-\frac{2}{3}}$$

The magnitudes $\eta_1$ and $\eta_2$ contained in $\varepsilon$ are the limiting values which the coefficient of viscosity attains, the one when the vapour or gas is entirely decomposed by dissociation into simple molecules, the other when all the molecules are combined in pairs. Of these limiting values we can at most assume $\eta_1$ as known, since we put for it the value of the coefficient of viscosity which has been observed for carbonic acid under such circumstances that it may pass without question as a perfect gas, *i.e.* under low pressure at a sufficiently high temperature. The other limiting value, $\eta_2$, is, however, not known, and must, indeed, itself be calculated from the observations. Therefore $\varepsilon$, which depends on the ratio of these two limiting values, is unknown, and the same is true, therefore, of both the magnitudes $A$ and $B$ which occur in the formula.

These two magnitudes $A$ and $B$ depend not only on $\varepsilon$, which according to the theory ought to be constant, but also on the density $D$ of the completely dissociated gas. What unit we are to choose for the numerical value of this magnitude is on the theory entirely at our pleasure; we can take the density of any gas whatever, such as atmospheric air, as unit, or we are equally at liberty to refer the number to the density of water as unit; it is only necessary that for both $\delta$ and $D$ one and the same unit should be chosen. Since Warburg and von Babo refer the density $\delta$ of the carbonic acid which they have themselves measured to that of water as unit, we must also choose this unit for $D$ if we wish to employ directly the values which they have tabulated and which they have denoted by $s$.

Doubts, however, may be raised whether $D$ is not variable with the pressure, and as to the law of variation, if variation does occur. Since $D$ denotes the density of the gas when all its molecules are decomposed into simple ones, we might be inclined to assume that the gas then behaves as a perfect gas, and therefore conforms to Boyle's law. In this case the density $D$ must be assumed to be proportional to the pressure, so that we may put

$$A = ap, \quad B = bp^{\frac{1}{2}},$$

where $a$ and $b$ are independent of the pressure, and therefore can be variable with the temperature only.

The assumption that the gas obeys Boyle's law appears, however, as very improbable if we remember that the temperature in the experiments lay between 25° and 41°, and was, therefore, on neither side very different from the critical temperature 31°, at which, under certain circumstances, the distinction between liquid and gaseous carbonic acid ceases. Instead of Boyle's law, therefore, we might with equal justice assume that the density of the carbonic acid vapour varies but very little with the pressure, just like that of any liquid. That this assumption is for the most part really satisfied under the circumstances of Warburg and von Babo's experiments is seen from the observations of Andrews on the continuity of the gaseous and liquid states, being especially perceptible from the curves which are given in his memoir.[1] These show the volume of the partly gaseous and partly liquid carbonic acid to be nearly constant at temperatures which are very near to those employed by Warburg and von Babo, and under similarly high pressures; whence it follows that the density of the carbonic acid vapour is nearly equal to that of liquid carbonic acid, and that therefore, under the circumstances now coming into consideration, they are both independent of the pressure.

I have therefore calculated the results of the observations communicated by Warburg and von Babo[2] under both assumptions, supposing in the first place that Boyle's law is obeyed and in the second that the density $D$ is invariable.

The results of the calculations gave that at 25·1°, the lowest temperature employed by Warburg and von Babo, their observations are quite unrepresentable by the formula with variable values of $D$, $A$, and $B$, and that, on the contrary, the assumption of the values

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[1] *Phil. Trans.* 1869, clix. p. 575; *Pogg. Ann.* Erg.-Bd. v. p. 64, 1871.

[2] Table xii. of their complete memoir; p. 512 of the extract.

$$A = 1{\cdot}203, \quad B = 0{\cdot}000378,$$

which I have found as mean values, is very satisfactory. For the values of the coefficient of viscosity, which are calculated from the formula

$$\eta = 0{\cdot}000378\, \delta^{\frac{1}{2}}\, (1{\cdot}203 - \delta)^{-\frac{2}{3}}$$

with the values of $\delta$ given by Warburg and von Babo, agree very well with those observed, as the following table shows :—

*Carbonic Acid at* 25·1°.

| $p$ Atmospheres | $\delta$ | $\eta$ |  | Differences |
|---|---|---|---|---|
|  |  | Observed | Calculated |  |
| 105 | 0·896 | 0·000800 | 0·000786 | + 14 |
| 95 | 875 | 741 | 743 | − 2 |
| 85 | 858 | 703 | 712 | − 9 |
| 75 | 827 | 665 | 660 | + 5 |
| 70 | 809 | 628 | 632 | − 4 |

When I attempted to calculate in like manner the other numbers[1] obtained at higher temperatures, I found for the magnitude $A$ values which were so little greater than that already found, viz. 1·203, that I thought I might assume this value for all the series of experiments. I thus obtained the following values for $A$ and $B$ at the temperatures named :—

$\vartheta = 25{\cdot}1$ $\quad A = 1{\cdot}203$ $\quad B = 0{\cdot}000378$
32·6 1·203 398
35 1·203 409
40·3 1·203 404

Whether and how far the values of $\eta$ calculated from the formula with these values agree with the observed values is shown by the following table :—

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[1] I have submitted to calculation only those results of observation in which the amount of air mixed with the carbonic acid was as small as possible.

*Carbonic Acid.*

| $\vartheta$ | $p$ Atmospheres | $\delta$ | $\eta$ Observed | $\eta$ Calculated | Differences |
|---|---|---|---|---|---|
| 32·6 | 107·3 | 0·800 | 0·000677 | 0·000652 | + 25 |
| | 88·5 | 730 | 574 | 560 | + 14 |
| | 80·7 | 660 | 493 | 486 | + 7 |
| | 78·2 | 590 | 414 | 424 | − 10 |
| | 77·6 | 520 | 351 | 370 | − 19 |
| | 77·2 | 450 | 304 | 323 | − 19 |
| | 76·6 | 380 | 270 | 279 | − 9 |
| | 74·6 | 310 | 239 | 239 | 0 |
| | 69·9 | 240 | 213 | 200 | + 13 |
| | 60·3 | 170 | 188 | 161 | + 17 |
| 35 | 96·2 | 0·730 | 0·000576 | 0·000575 | + 1 |
| | 87·6 | 660 | 500 | 499 | + 1 |
| | 83·8 | 590 | 431 | 435 | − 4 |
| | 82·1 | 520 | 367 | 380 | − 13 |
| | 81·2 | 450 | 322 | 331 | − 9 |
| | 79·8 | 380 | 289 | 287 | + 2 |
| | 77·2 | 310 | 247 | 245 | + 2 |
| | 71·6 | 240 | 217 | 205 | + 12 |
| | 61·4 | 170 | 193 | 165 | + 28 |
| | 43·9 | 100 | 177 | 121 | + 56 |
| 40·3 | 114·6 | 0·730 | 0·000580 | 0·000569 | + 11 |
| | 101·6 | 660 | 499 | 494 | + 5 |
| | 94·9 | 590 | 426 | 430 | − 4 |
| | 91·7 | 520 | 366 | 376 | − 10 |
| | 89·2 | 450 | 316 | 328 | − 12 |
| | 86·8 | 380 | 275 | 284 | − 9 |
| | 82·7 | 310 | 243 | 243 | 0 |
| | 75·9 | 240 | 218 | 203 | + 15 |
| | 64·3 | 170 | 196 | 163 | + 33 |
| | 45·3 | 100 | 180 | 120 | + 60 |

I then calculated the same observations by the formula

$$\eta = b p^{\frac{1}{6}} \delta^{\frac{1}{2}} (ap - \delta)^{-\frac{2}{3}},$$

on the assumption that $a$ and $b$ are independent of the pressure $p$. This formula, as has been mentioned, would not apply to the temperature 25·1° ; for the other temperatures, on the contrary, I found

| | | |
|---|---|---|
| $\vartheta = \cdot 6$ | $a = 0{\cdot}01332$ | $b = 0{\cdot}0001734$ |
| 35 | 1374 | 1859 |
| 40·3 | 1142 | 1665 |

and with these values I calculated from the formula the following values of the coefficient of viscosity which, as before, I tabulate opposite those observed :—

*Carbonic Acid.*

| $\vartheta$ | $p$ Atmospheres | $\delta$ | $\eta$ |  | Differences |
|---|---|---|---|---|---|
|  |  |  | Observed | Calculated |  |
| 32·6 | 107·3 | 0·800 | 0·000677 | 0·000460 | +217 |
|  | 88·5 | 730 | 574 | 534 | + 40 |
|  | 80·7 | 660 | 493 | 526 | − 33 |
|  | 78·2 | 590 | 414 | 468 | − 54 |
|  | 77·6 | 520 | 351 | 403 | − 52 |
|  | 77·2 | 450 | 304 | 346 | − 42 |
|  | 76·6 | 380 | 270 | 296 | − 26 |
|  | 74·6 | 310 | 239 | 255 | − 16 |
|  | 69·9 | 240 | 213 | 221 | − 8 |
|  | 60·3 | 170 | 188 | 192 | − 4 |
| 35 | 96·2 | 0·730 | 0·000576 | 0·000482 | + 94 |
|  | 87·6 | 660 | 500 | 478 | + 22 |
|  | 83·8 | 590 | 431 | 439 | − 8 |
|  | 82·1 | 520 | 367 | 389 | − 22 |
|  | 81·2 | 450 | 322 | 340 | − 18 |
|  | 79·8 | 380 | 289 | 297 | − 8 |
|  | 77·2 | 310 | 247 | 259 | − 12 |
|  | 71·6 | 240 | 217 | 226 | − 9 |
|  | 61·4 | 170 | 193 | 198 | − 5 |
|  | 43·9 | 100 | 177 | 175 | + 2 |
| 40·3 | 114·6 | 0·730 | 0·000580 | 0·000452 | +128 |
|  | 101·6 | 660 | 499 | 464 | + 35 |
|  | 94·9 | 590 | 426 | 427 | − 1 |
|  | 91·7 | 520 | 366 | 391 | − 25 |
|  | 89·2 | 450 | 316 | 344 | − 28 |
|  | 86·8 | 380 | 275 | 300 | − 25 |
|  | 82·7 | 310 | 243 | 262 | − 19 |
|  | 75·9 | 240 | 218 | 224 | − 6 |
|  | 64·3 | 170 | 196 | 201 | − 5 |
|  | 45·3 | 100 | 180 | 178 | + 2 |

If we compare the numbers in these tables with each other we at once notice a certain contrast in the behaviour of the numbers as calculated by the two formulæ. For smaller values of the pressure which lie below 70 atmospheres, only the formula with variable $A$ and $B$ is satisfactory, the other with constant $A$ and $B$ being certainly not. At higher pressures, however, the formula with constant $A$ and $B$ corresponds with the observations very much better than the other, which gives values that deviate widely from the truth.

We must therefore conclude that carbonic acid at temperatures between 30° and 40° obeys the laws of perfect gases with sufficient accuracy so long as the pressure remains below a limit of about 70 atmospheres, which corresponds nearly to the critical pressure. But if the pressure exceeds this limit, carbonic acid behaves, at least approximately, like a liquid the density of which is scarcely altered by pressure.

Since this behaviour is confirmed also by observations of another kind, we may look on the result of our calculations as a sign that the theory of the viscosity of partially dissociated gases developed in § 89 is substantially founded on truth. We shall have to assume that the formula

$$\eta = B\delta^{\frac{1}{2}}(A - \delta)^{-\frac{2}{3}}$$

really represents the coefficient of viscosity of a partially dissociated gas of density $\delta$, and $A$ and $B$ are to be looked upon as constants if the pressure is sufficiently high, but to be put

$$A = ap, \ \ B = bp^{\frac{1}{6}}$$

for smaller values of the pressure $p$, $a$ and $b$ being constants.

I might probably have found a general formula applicable to all values of the pressure if I had attempted to use as basis of my calculations one of the general laws which have been proposed by van der Waals, Clausius, and others to represent the connection between the pressure and the density. I have had to abandon doing this, as I wished to delay the appearance of this book no longer.

## 91. Viscosity of the Perfectly-dissociated Gas and of the Non-dissociated Gas

I have, on the other hand, sought for a more comprehensive proof of the theoretical formula by returning to the theoretical meaning of the magnitudes $A$ and $B$, the values of which I have obtained from the observations, and investigating the conclusions of another kind to which they lead. According to § 90,

$$A = D(2 - \varepsilon)/(1 - \varepsilon), \ \ B = \eta_1 D^{\frac{1}{6}}(1 - \varepsilon)^{-\frac{2}{3}},$$

where $\varepsilon$ is determined by the ratio of the two limiting values of the coefficient of viscosity, viz. $\eta_1$ of the gas when completely dissociated into simple molecules $CO_2$ and $\eta_2$ of the gas when composed of only the double molecules $C_2O_4$, in accordance with the formula

$$\varepsilon = 2^{\frac{3}{4}}(\eta_1/\eta_2)^{\frac{3}{2}}.$$

$D$ is further the density which the gas would possess under the circumstances of the experiment if it were entirely dissociated into simple molecules.

The three magnitudes $\eta_1$, $\eta_2$, $D$ named above are not capable of direct measurement because we cannot know whether the limiting case in which the gas contains only molecules of one kind, single or double, has been reached in any experiment.

But from one of the laws of theoretical chemistry[1] we can theoretically calculate the density $D$ of a gas from its molecular weight. Since now, according to what we have already said, carbonic acid below the critical pressure, or at least below 70 atmospheres, may be considered as an actual gas, we are justified in extending the procedure for the calculation of $D$ to the formulæ in which we put

$$A = ap, \;\; B = bp^{\frac{1}{3}}.$$

We may therefore put these formulæ in the shape

$$a = \Delta(2-\varepsilon)/(1-\varepsilon), \;\; b = \eta_1\Delta^{\frac{1}{3}}(1-\varepsilon)^{-\frac{2}{3}},$$

wherein

$$\Delta \equiv D/p$$

represents the density of the completely dissociated gas under the pressure of 1 atmosphere, and therefore the known magnitude which chemists call the *theoretical* or *normal* density of the gas. We have now to take into account the circumstance that we must retain for its specification the unit of density assumed by Warburg and Von Babo, so that we must not take for carbonic acid the usual value 1·5198 as referred to air, but its value as calculated with the density of water for unit, for which we obtain at the temperature of freezing-point

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[1] § 30.

$$\Delta_0 = 1{\cdot}5198/773{\cdot}3 = 0{\cdot}0019653$$

and at the temperature $\vartheta$

$$\Delta = 0{\cdot}0019653/(1 + a\vartheta),$$

where $a = 0{\cdot}00367$ is the coefficient of expansion.

If we put this value of $\Delta$ in the formula for $a$, we obtain from the given values of $a$, first the corresponding values of

$$\varepsilon \equiv 2^{\frac{3}{4}}(\eta_1/\eta_2)^{\frac{3}{2}},$$

and thence those of the ratio which the two coefficients of viscosity bear to each other :—

| | | |
|---|---|---|
| $\vartheta = 32{\cdot}6$ | $\varepsilon = 0{\cdot}8482$ | $\eta_1/\eta_2 = 0{\cdot}634$ |
| 35 | 8550 | 637 |
| 40·3 | 8236 | 621 |

If we now employ the formula for $b$ in the same way we find also the absolute values of the two coefficients of viscosity, firstly that of $\eta_1$ for the gas when perfectly dissociated into the simple molecules $CO_2$, and then that of $\eta_2$ for the gas when containing only the double molecules $C_2H_4$, thus,

| | | |
|---|---|---|
| $\vartheta = 32{\cdot}6$ | $\eta_1 = 0{\cdot}000142$ | $\eta_2 = 0{\cdot}000224$ |
| 35 | 148 | 232 |
| 40·3 | 151 | 244 |

These numbers refer to the temperatures placed opposite them. I have therefore reduced them to 0° C. by assuming for $CO_2$ the temperature-factor

$$1 + a\vartheta,$$

which holds approximately (§ 85) for ordinary carbonic acid, and, on the contrary, for $C_2O_4$ the temperature-function

$$(1 + a\vartheta)^{\frac{3}{2}},$$

which holds for vapours (§ 87). I have thus obtained for the temperature 0° C. the following values :—

| | |
|---|---|
| $\eta_1 = 0{\cdot}000127$ | $\eta_2 = 0{\cdot}000189$ |
| 131 | 194 |
| 132 | 198 |

which exhibit a fairly satisfactory agreement.

A comparison of these values with those obtained for the viscosity of carbonic acid under ordinary pressures is obviously the next thing. As was mentioned before, in § 79, Graham's experiments on carbonic acid at 0° gave $\eta = 0{\cdot}000145$; Puluj found the nearly equal value $\eta = 0{\cdot}000143$, while von Obermayer and Schumann agree in finding the rather smaller value $\eta = 0{\cdot}000138$; [and the mean of all these is

$$\eta = 0{\cdot}000141].$$

Since this is only slightly greater than the mean value

$$\eta_1 = 0{\cdot}000130$$

now found for perfectly dissociated carbonic acid, the assumption that carbonic acid under ordinary circumstances consists almost entirely of simple molecules $CO_2$, seems to be justified.

Nearly the same results are deducible also from the formulæ which contain constant values of $A$ and $B$, if we make an assumption regarding the variation of the density with the pressure such as after our former explanations cannot be taken as entirely improbable. I assume that the density of gaseous carbonic acid obeys Boyle's law up to the critical pressure, which is 77 atmospheres according to Andrews[1]; from this limit onward, however, I assume the density not to be variable with the pressure. In reality there will certainly be a continuous change from the one state to the other, but I think that we may take this assumption to be allowable as an approximation to the true behaviour.

I therefore put for the density of the intensely compressed gas which has become independent of the pressure the value

$$D = 77 \times 0{\cdot}0019653/(1 + a\vartheta) = 0{\cdot}15133/(1 + a\vartheta),$$

wherein $\vartheta$ is the temperature and $a$ the coefficient of expansion 0·00367. On putting this value in the formula

$$A = D(2-\varepsilon)/(1-\varepsilon)$$

---

[1] *Phil. Trans.* 1876, clxvi. p. 421.

where $A$ has the value

$$A = 1{\cdot}203,$$

which was found to be the same in all the series of observations, we find for the four temperatures of the observations 25·1°, 32·6°, 35°, 40·3° the nearly agreeing values 0·870, 0·876, 0·875, 0·877, respectively for $\varepsilon$, the mean of which is

$$\varepsilon \equiv 2^{\frac{3}{4}}(\eta_1/\eta_2)^{\frac{3}{2}} = 0{\cdot}874,$$

from which further follows

$$\eta_1/\eta_2 = 0{\cdot}6465,$$

so that the ratio in this case only slightly exceeds that resulting from the other calculation [viz. 0·631 in the mean].

We further obtain the following values of $\eta_1$ from the values given before for $B$:—

$$\begin{array}{rllll} \vartheta = & 25{\cdot}1 & 32{\cdot}6 & 35 & 40{\cdot}3 \\ B = & 378 & 398 & 409 & 404 \\ 10^6\eta_1 = & 131{\cdot}9 & 139{\cdot}4 & 143{\cdot}4 & 142{\cdot}3\,; \end{array}$$

and on reducing these to 0° C. by division by $1 + a\vartheta$, we get for $10^6\eta_1$ the values 121, 124, 127, 124 respectively. These give values of $\eta_1$ that are somewhat smaller than the former mean value 0·000130, but they do not vary very much from their mean value

$$\eta_1 = 0{\cdot}000124.$$

From this follows for the coefficient of viscosity of the gas at 0° when all its molecules are double, or $C_2O_4$, the value

$$\eta_2 = 0{\cdot}000192$$

which agrees perfectly with the mean ( 0·000194 ) of the numbers found for it from the other formula.

After this multiplied confirmation of our formulæ we can scarcely still doubt that the theory of viscosity in partially dissociated gases which we have developed corresponds to the reality in all essential points. The deviations which occur between calculation and observation will doubtless be completely explained and made to disappear when the calculation is made with more exactness and generality.

A first improvement that is desirable has already been named; it consists in the introduction of a law of dependence of the density on the pressure, which embraces both the liquid and the gaseous states of the substance. A second possibility of improving the theory lies in the consideration that, in addition to single molecules $CO_2$ and double ones $C_2O_4$ in the gas, there may also be present triple molecules $C_3O_6$, quadruple ones $C_4O_8$, &c.

The want of the necessary leisure alone prevents me from carrying out these calculations.

## 92. Transition into the Critical State

In the combination of the simple molecules of a gas or vapour to form larger masses we must doubtless see an approximation to the liquid state in which all particles are joined together into one cohering mass. If, now, the viscosity increases when the density rises by aggregation of the molecules, as in the theories and observations we have before discussed, we shall have to conclude that the viscosity of a vapour attains its greatest value when the vapour has attained the saturated state.

But an experiment of Lothar Meyer's,[1] on the viscosity of the vapour of benzol, seems to contradict this. He allowed saturated benzol vapour to pass through a capillary tube into a space where the pressure was less; the vapour was here condensed by cooling, and the mass of vapour which had traversed the capillary tube in a given time was determined by weighing the liquid. From this weight the coefficient of viscosity of the vapour was calculated by Poiseuille's law. Calculation gave the value of this coefficient (which is constant for gases) to be the smaller the higher the back pressure at the exit of the capillary tube. We may therefore also say that the friction seemed to be the smaller the larger the mean pressure was in the tube; but this is the exact opposite of the theoretical conclusion, that the viscosity of a vapour is the more considerable the nearer the vapour is to the saturated state.

Lothar Meyer has explained this apparent contradiction in an easy way, by recalling attention to the fact that the saturated vapour which enters the tube cannot, with a high back-pressure, expand so much as still to follow with sufficient exactness the gaseous laws, while, with smaller back-pressure, it is brought by expansion still more nearly into the state of a perfect gas. Schumann,[1] who had taken part in carrying out these observations, followed up this explanation still further by saying outright that the originally saturated vapour must, during its expansion, form drops of liquid which it carries on with it, and that thence it follows that the mass transpired comes out as too great, and consequently the coefficient of viscosity as too small.

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[1] *Wied. Ann.* 1879, vii. p. 531.

To make this explanation of the process perfectly clear and convincing we have only to remember that a saturated vapour which expands must cool thereby, and consequently partially condense into a liquid. The capillary tube used in Lothar Meyer's experiments was, of course, contained in a tube surrounded by the vapour of benzol of the same pressure and temperature, so that it seemed to be ensured against cooling. But if we consider that the thick wall of a fine capillary tube offers a considerable obstruction to the passage of heat, it in no way seems improbable that a slight lowering of the temperature might have occurred within the capillary tube, and that, therefore, a slight amount of vapour might have been condensed. This mass of vapour precipitated in the form of drops will then settle on the walls of the tube, and spread over them as a thin liquid layer.

That the transpired mass becomes greater by means of this disturbance of the experiment follows at once from the fact that the density of the liquid is very much greater than that of the vapour. But we might raise the objection that the friction which the liquid experiences as it flows along the bottom of the tube is also much greater than that which the vapour undergoes. This objection is, however, answered by the fact that the coefficient of friction of a substance is not by any means so greatly altered by the passage from the vapour into the liquid state as its density is. Thus, for instance, the coefficient of friction of water in the liquid state at mean temperatures is only about 120 times greater than that of water-vapour, while the density of the liquid water is about 1,000 times greater than that of water-vapour under atmospheric pressure. From this example we easily understand how a wet vapour seems to have a smaller viscosity than a dry saturated vapour.

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[1] *Wied. Ann.* 1884, xxiii. p. 393.

This behaviour substantially occurs also in the case of mercury vapour, the viscosity of which has been determined by Synesius Koch. Since the mercury vapour entered into the capillary tube in a saturated state in Koch's experiments, we must assume that, in these measures too, some of the vapour condensed in the tube into little drops, and that, consequently, the transpired masses came out too large, and, therefore, the values of the viscosity too small[1]; and, indeed, they will have come out the smaller the nearer the vapour was to condensing, and, therefore, the lower its temperature. Hence the consequence would be that the observations would give a greater variation of the viscosity with temperature than the theory could explain. The same might, in like manner, occur with many others of the vapours mentioned in § 87.

[1] Compare also § 108.

# CHAPTER VIII

## *DIFFUSION OF GASES*

### 93. Observations

By diffusion we understand the slow mixing of two liquids or gases which were previously separated. Such mixing may be effected by processes of different kinds which, though closely connected, are yet so materially different from each other that it is well to give them different names. In this the terminology of Graham is satisfactory.

When the two substances are separated by a solid wall which contains one or more narrow openings, the mixing is caused by *effusion*, the laws of which have already been discussed in Chapter III. § 37. This mode of mixing must be distinguished from that which takes place through the pores of a natural or artificial membrane, a porous pot or the like, which for liquids is called *osmose*, and for gases *transpiration*; the slowness with which this transpiration is carried on is a consequence of the internal friction of the gas, dealt with in Chapter VII., which is active within the narrow channels of the porous partition. A process which essentially differs from the last is that which occurs when the substance of the partition is capable of absorbing either one or both of the gases, so that it takes the gas in at one side and gives it out at the other; this process can also be explained by the kinetic hypothesis, but as it is conditioned, not only by the state of motion of the gaseous substance, but also by the movements of the molecules of the liquid or solid partition, we cannot treat of it here. What we have here to describe, viz. diffusion in the narrower sense of the word, is the mixing together of two liquids or gases which directly touch each other without being hindered by a partition. The explanation of the extreme slowness of this free diffusion between gases is now the special problem before us.[1]

Passing over the older observations of Dalton,[2] Berthollet,[3] Graham,[4] and others, I choose, as instances, the experiments carried out by Loschmidt[5] on the diffusion of gases.

A glass tube, 975 mm. long and of 26 mm. diameter, which can be closed at both ends by flat glass plates and glass stopcocks, was cut into two parts of equal lengths, which could at will be shut off from each other or put into connection by means of a slider made of a thin sheet of steel in which was a hole as large as the inner section of the tube. After the two halves had been filled with different gases under the same pressure, the slider was opened so that the gases began to mix, and after the lapse of a measured time—from half an hour to an hour—the slider was again closed, and the gas in each half of the tube was then analysed in order to determine the degree to which the mixing had progressed during the time of the experiment, and from this to discover the speed of diffusion.

A theory developed by Stefan[6] was employed for the reduction of these experiments. This starts with the assumption, made also by Maxwell[7] and Boltzmann,[8] of the idea of a *resistance to diffusion* which each gas experiences from the particles of the other gas which meet it. This resistance is taken to be proportional to the densities of both gases and to the difference of their speeds of diffusion. The working out of this idea leads to formulæ which have a great likeness to the equations which come into Fourier's theory of the conduction of heat.

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[1] We must not conclude that, because Thos. Graham so judiciously distinguished these differing phenomena by different names, he was the first to employ these names. The term *diffusion* was used by Dalton ('On the Tendency of Elastic Fluids to Diffuse through Each Other,' *Mem. Manch. Soc.* 1805, new series, i. p. 244) and Priestley (*Trans. Amer. Phil. Soc.* 1802, v. p. 15; 'Experiments and Observations relating to Various Branches of Natural Philosophy,' Birmingham 1781, iii. sect. 27, § 3, p. 390.

[2] In different places; *Gilb. Ann.* 1807, xxvii. p. 388.

[3] *Mém. d'Arcueil*, 1809, ii. p. 463.

[4] *Quarterly Journ. of Sc. Lit. and Art*, 1829, p. 74; *Pogg. Ann.* 1829, xvii. p. 375.

[5] 'Experimentaluntersuchungen über die Diffusion von Gasen ohne poröse Scheidewände,' *Wien. Sitzungsber.* Abth. 2, 1870, lxi. p. 367; lxii. p. 468; continued by Wretschko, lxii. p. 575; and by Benigar, lxii. p. 687.

[6] *Wiener Sitzungsber.* Abth. 2, 1871, lxiii. p. 63; 1872, lxv. p. 323.

[7] *Phil. Mag.* [4] 1860, xx. p. 21; 1868, xxxv. p. 199. *Scientific Papers*, i. p. 392; ii. p. 57.

[8] 'Weitere Studien u.s.w.' *Wien. Sitzungsber.* Abth. 2, 1872, lxvi. p. 324; 1878, lxxviii. p. 733; 1882, lxxxvi. p. 63; 1883, lxxxviii. p. 835.

This similarity is not only in respect of the mathematical form, but is founded on the nature of the matter. Just as heat spreads in a conducting body, so in diffusion a gas spreads from one region to another. The speed with which heat is transmitted is determined for each substance by a constant which is termed the *conductivity*; in like manner the speed with which one gas penetrates into another is determined by a magnitude which we might call the *diffusivity*, but which is more usually termed the *coefficient*, or *constant*, *of diffusion*.

The meaning of these two constants is quite analogous. We obtain the strength of the flow of heat by multiplying by the conductivity the difference of the temperatures at two places, which are distant from each other by unit length along the line of flow, *i.e.* the so-called rate of fall of temperature. We likewise obtain the intensity of the flow of diffusion if we multiply by the coefficient of diffusion the difference of the density of the diffusing gas at two places whose distance apart is equal to unit length. But we can express the meaning of this coefficient also in a somewhat different way by replacing the density by the pressure which, by Boyle's law, is proportional to it. We may then say that the amount of partial pressure of one of the gases transmitted by the diffusion is given by the difference in the values of this partial pressure at two places which are separated by unit length (or, as we may say more shortly, by the rate of fall of the partial pressure), multiplied by the coefficient of diffusion.

From this determination of the flow of diffusion it is easy to see that the coefficient, which holds for the diffusion of one gas into any other, must be equal to that upon which the diffusion of the second gas into the first depends. For since no inequality in the total pressure is brought about by diffusion in an experiment wherein the initial pressures of the two diffusing gases are equal to each other, the strengths of the two flows which occur in opposite directions, but otherwise under the same circumstances, must be equal, and, therefore, also the two coefficients must be equal.

Loschmidt's observations showed that the value of this coefficient is inversely proportional to the total pressure of the gases, so that, as is almost obvious, the mixing occurs the more rapidly the more rarefied the gases. Loschmidt found further that the coefficient alters with the temperature in accordance with the law, that it increases nearly proportionally to the square of the absolute temperature. Finally it appeared that a regular relation must exist with the molecular weights, which, however, did not succeed in disclosing itself with full clearness.

We have to develop the value of this coefficient from the conceptions of the kinetic theory.

## 94. General Theory of Diffusion

The slowness with which two diffusing gases mix together is to be explained on the kinetic hypothesis in a way which is so fully analogous to the conceptions underlying the theory of friction that we may speak of diffusion as a kind of reverse friction of the two gases on each other.

The cause of the phenomenon, that the forward flow of one layer is transmitted only very slowly by friction to a distant layer, lies only in the shortness of the molecular path. With all their swiftness of motion, the molecules transmit a part of their own momentum only to those particles that are quite close to them and with which they collide after traversing a very short path. A transference of momentum to a greater distance takes place, therefore, only by the interaction of very many particles in their to-and-fro motions; it is, consequently, carried on by no means in a straight direction, and experiences, therefore, a considerable retardation, which appears to us as a consequence of friction.

The proof that the shortness of the molecular paths must cause an equal slowness in the mixing or diffusion of two gases may be deduced in an exactly corresponding way. This is just the point on which Clausius[1] laid special stress in his celebrated memoir on the free paths of molecules. Into a space already filled with one gas the molecules of a second gas penetrate only slowly, because by their frequent collisions with the molecules of the first gas they are driven hither and thither, so that it is impossible for them, even with their enormous speed, to penetrate into the interior of the other mass in straight lines.

The velocity of diffusion therefore depends not only on the speeds with which the molecules of the diffusing gases move, but also no less on the length of the free path which a molecule of one sort traverses among molecules of the other sort. It is thus conditioned by the same elements as the friction of gases, viz. molecular speed and free path.

A closer examination of the way in which these two elements are connected together leads to a knowledge of the value of the coefficient of diffusion and teaches us to see its meaning and its relations to other magnitudes.

## 95. Theoretical Value of the Coefficient of Viscosity

At each moment during the interval occupied by an experiment the diffusing gases may be in such a state of motion that the equilibrium of the total pressure exerted by the mixture is nowhere disturbed; there is then at every point the same pressure $p$, and this is the sum of the partial pressures $p_1$ and $p_2$ which each of the two gases would exert by itself, or

$$p = p_1 + p_2.$$

Similarly, by Avogadro's law, there is the same number of molecules in each unit volume, which we will represent by

$$N = N_1 + N_2,$$

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[1] *Pogg. Ann.* 1858, cv. p. 239; *Abhandlungen*, Abth. 2, 1867, p. 260; *Phil. Mag.* 1858 [4] xvii. p. 81.

where $N_1$ and $N_2$ are put for the number of molecules of the first and second sort in the unit volume.

But the mixture is not homogeneous; the nearer to one end of the tube, the more in excess are the molecules of one kind, just as those of the other kind are at the opposite end. The pressure and density of one gas diminish along the tube in one direction, while those of the other gas increase in the same direction in equal measure. If the experiment has already lasted some time, the diminution of pressure all along the tube will have become uniform, so that we can represent the pressure and the number of particles of the one gas at the distance $x$ from the junction of the diffusion-tubes by formulæ of the form

$$p_1 = \mathfrak{P} + \mathfrak{p}x\,,\quad N_1 = \mathfrak{N} + nx,$$

while the same magnitudes for the other gas are

$$p_2 = p - \mathfrak{P} - \mathfrak{p}x\,,\quad N_2 = N - \mathfrak{N} - nx.$$

Here the magnitude $\mathfrak{p}$ which determines the increase and decrease of the partial pressures is the same for our problem as what is called in hydraulics the slope of pressure, or the diminution of pressure in unit length along a line of flow. The analogous magnitude $n$ determines the decrease or increase of density along the same length; it will result, in agreement with the views mentioned in § 93, that the strength of the diffusion-flow is proportional to it.

If such a uniform distribution of pressure and density has not yet been established along the whole tube, the foregoing simple formulæ can still be employed without error, if we use them for only a very short portion of the tube, and therefore, for instance, if by $x$ we understand a length which is shorter than a molecular free path, as in the following calculation.

We have to determine how many particles of each kind cross any section of the tube in a given time in consequence of the inequality of the pressure and density that has been described, or, more correctly, how many more cross in one direction than in the other. If the distribution were uniform, the number of particles which in unit time meet unit area of a section from one side and pass through it, would by § 82 be

$$\tfrac{1}{4}N_1\Omega_1 \text{ and } \tfrac{1}{4}N_2\Omega_2$$

for the two sorts of molecules, whose mean speeds are $\Omega_1$ and $\Omega_2$ respectively.

In consequence of the unequal distribution there come fewer particles of the first kind from the side of the smaller $x$ and more in the opposite direction, while for the other gas the reverse holds good. The particles of both groups start from layers which are distant from the section with abscissa $x$ by magnitudes that are less than the possible values of the free path, or are at most equal to them. The average distance of these starting layers from the section considered will be less than the mean free path, since a larger part of the particles not only reach this section but pass through it.

If we denote by $\Delta_1$ the value of this mean distance of the layers from which the particles of the first gas that cross the section come—and this value we shall determine later—those which cross in the positive direction start from layers which, on an average, are distant by $x - \Delta_1$ from the origin of the tube; the density in these layers is not determined by $N_1$ but only by

$$\mathfrak{N} + n(x - \Delta_1) = N_1 - n\Delta_1$$

particles in unit volume. From this side, therefore, there are only

$$\tfrac{1}{4}(N_1 - n\Delta_1)\Omega_1$$

particles of the first kind which in unit time meet unit area of the section; there similarly cross this unit area in the same time from the opposite side the number

$$\tfrac{1}{4}(N_1 + n\Delta_1)\Omega_1$$

of the same kind, which start, on the average, from the distance $x + \Delta_1$ from the origin of the tube. There is consequently an excess of

$$\tfrac{1}{2}n\Delta_1\Omega_1$$

particles of the first kind which in unit time cross unit area in the negative direction—*i.e.* towards the origin of the tube —more than in the opposite direction.

There are, similarly, more particles of the second kind which cross the same surface in the same time, but in the positive direction from the beginning of the tube, than in the opposite direction, and the number representing this excess is

$$\tfrac{1}{2}n\Delta_2\Omega_2,$$

where $\Delta_2$ has a meaning corresponding to that of $\Delta_1$.

Through this double flow the number of particles on the side of the section towards the origin increases by

$$\tfrac{1}{2}n(\Delta_1\Omega_1 - \Delta_2\Omega_2),$$

and thus an inequality of pressure arises which at once disappears again by causing

$$\tfrac{1}{2}n(\Delta_1\Omega_1 - \Delta_2\Omega_2)$$

particles of the mixture, and thus

$$\tfrac{1}{2}n(\Delta_1\Omega_1 - \Delta_2\Omega_2)N_1/N \quad \text{and} \quad \tfrac{1}{2}n(\Delta_1\Omega_1 - \Delta_2\Omega_2)N_2/N$$

particles of the two kinds respectively to cross the section towards the end of the tube.[1]

The number of particles, therefore, of the first kind which finally diffuse in unit time over unit area towards the origin of the tube is

$$\tfrac{1}{2}n\Delta_1\Omega_1 - \tfrac{1}{2}n(\Delta_1\Omega_1 - \Delta_2\Omega_2)N_1/N$$
$$= \tfrac{1}{2}n(N_2\Delta_1\Omega_1 + N_1\Delta_2\Omega_2)/N.$$

The oppositely directed diffusion of the second gas has the same strength, for it is

$$\tfrac{1}{2}n\Delta_2\Omega_2 + \tfrac{1}{2}n(\Delta_1\Omega_1 - \Delta_2\Omega_2)N_2/N$$
$$= \tfrac{1}{2}n(N_1\Delta_2\Omega_2 + N_2\Delta_1\Omega_1)/N.$$

From this number of the particles which cross unit area in unit time we obtain the change of the partial pressure of each of the two gases which is due to them directly expressed by the formula

$$\tfrac{1}{2}\mathfrak{p}(N_2\Delta_1\Omega_1 + N_1\Delta_2\Omega_2)/N,$$

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[1] Gross contests, wrongly, as I think, the correctness of this conclusion. *Wied. Ann.* 1890, xl. p. 424.

since the pressure is always directly proportional to the number of particles which give rise to it, and therefore the excess of pressure $\mathfrak{p}x$ is proportional to the surplus number of particles $nx$, or $\mathfrak{p}$ to $n$.

Our theory is now so far developed that the strength of the diffusion-current has been expressed in terms of the numbers $n$ and $\mathfrak{p}$, which give the measure of the inequality of the distribution. We thereby find an analogy, already hinted at, with the flow of heat that is caused by inequality in the distribution of temperature, which is so far confirmed as touches the proportionality in both cases of the flow to the surplus that is present. We therefore define as *the coefficient of diffusion* the factor of proportionality

$$D \equiv (N_1\Delta_2\Omega_2 + N_2\Delta_1\Omega_1)/2N.$$

We have still in this formula to determine more closely the two distances denoted by $\Delta$. We have already said that they are smaller than the mean free paths of the molecules. The determination of the numerical ratio in which they are less than the free paths is of secondary importance. We easily see without calculation that $\Delta$ must for every gas be about half as large as the mean free path of its molecules; for the path on which a particle crosses the plane considered will lie, on an average, half on the one side of the plane and half on the other. But since the more rapidly moving particles attain a greater free path than the slower ones, the more rapid particles will exert a greater influence on the value of the product $\Delta\Omega$; by an accurate calculation, therefore, we may expect to find a rather larger value for the ratio of $\Delta$ to the mean free path. As a matter of fact, we find by a calculation founded on Maxwell's law of distribution of speeds, and given in § 52* of the Mathematical Appendices, that the ratio of $\Delta$ to the free path is equal to $\frac{1}{4}\pi$. The formula for the coefficient of diffusion therefore becomes

$$D = \tfrac{1}{8}\pi(N_1\mathfrak{L}_2\Omega_2 + N_2\mathfrak{L}_1\Omega_1)/N,$$

if we denote by $\mathfrak{L}_1$ and $\mathfrak{L}_2$ the free paths of the two kinds of molecules in the mixture, and in this form it exhibits a striking likeness to the value of a coefficient of viscosity.

There exists, however, an important difference between the two formulæ for the coefficients of viscosity and diffusion, which lies in the different significations of the molecular free paths. While in our discussions on viscosity we had to deal with only those paths which a molecule passes over in a crowd of molecules of the same kind, the question in the theory of diffusion concerns the lengths of the paths of a particle which moves among other particles not only of its own kind but also of another kind, and which collides with particles of both kinds. To calculate these free paths, therefore, we have to find the number of collisions of both kinds in unit of time.

Since we have already learnt how to determine the number of collisions of a particle by others of its own kind, it is now only necessary to calculate how often a particle collides with the particles which are present of another kind. We attain thereby at once the possibility of calculating the mean length of the paths which a single particle can traverse in a crowd of gaseous molecules of another kind.

## 96. Free Path of a Gaseous Molecule in a Gas of Different Kind

This calculation may be carried out in exactly the same manner as it is in Chapter VI. for the value of the free path of a molecule of a simple gas; and the calculation is so fully analogous to that simpler one that a complete repetition of it seems unnecessary; it will be sufficient to bring forward the distinguishing points of importance which have reference to the molecular sphere of action and the molecular speed.

The probability of a collision, or the frequency of the collisions, is proportional to the section of the sphere of action or to the area of the circle whose radius is equal to the distance between the centres of the two colliding molecules at the first moment of the encounter. This radius and this area must have different values for every different kind of gas, since the free path differs for different gases, as we have learnt from the observations on viscosity. We shall therefore not be justified, when considering the encounters between particles of different kinds, in taking the value of the radius that is proper to either the one or the other kind of gas, but we must introduce a third value of this radius, which we shall denote by the letter $\sigma$, to distinguish it from the symbol $s$ which we have before employed for a homogeneous gas. In the formula for the collision-frequency and for the free path we have therefore to replace the section $\pi s^2$ by $\pi\sigma^2$.

According to a suggestion made by Stefan,[1] which seems to be confirmed by experiment, the magnitude $\sigma$ stands in a simple relation to the two magnitudes $s_1$ and $s_2$, the values that hold for the two simple gases; this relation being probably

$$\sigma = \tfrac{1}{2}(s_1 + s_2).$$

The meaning of this equation is directly intelligible if we do not look upon the molecules as massive points, but ascribe to them the property of extension in space, and take $\frac{1}{2}s_1$ and $\frac{1}{2}s_2$ as the mean radii of the two kinds of molecules. The interpretation of the formula is, however, not bound up with this material conception, but it admits of a dynamical explanation; we may consider the molecules to be centres of force surrounded by spheres of force of radius $\frac{1}{2}s$, if we ascribe to the spheres of force the property of not suffering the one to penetrate into the other.[2]

The free path of a molecule of one gas in another gas will, in the second place, depend on the speeds of both kinds of molecules. To determine the character of this dependence, let us first for simplicity consider a gaseous medium whose molecules do not move to and fro in all possible directions of space, but only in directions which are perpendicular to those of the entering particle. These to-and-fro motions make the probability of a collision greater than it would be if the particle moved into a medium at rest; for a particle moving hither and thither will require a greater space for itself during the time in which the molecule wanders past it, and therefore comes more easily into the condition of colliding with it. The probability is increased in the same measure as the relative velocity of the two moving particles with respect to each other is greater than that of the particle moving alone. In the case supposed the magnitude of the relative velocity is easily obtained; the absolute velocities of the two particles (since they are perpendicular to each other) form the shortest pair of sides of a right-angled triangle, the hypotenuse of which represents the relative velocity of each with respect to the other. If these absolute velocities are represented by $\Omega_1$ and $\Omega_2$ as hitherto, the magnitude of the relative velocity is

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[1] *Wien. Sitzungsber.* 1872, lxv. Abth. 2, p. 323.

[2] Compare §§ 44, 63, 113.

$$\sqrt{(\Omega_1^2 + \Omega_2^2)}.$$

This consideration may be directly extended to the more general case such as really occurs. If the molecules do not move only at right angles to the particles coming in among them, but hither and thither in all possible directions, the probability of a collision is increased by this motion in exactly the same measure as by that to-and-fro motion which we have hitherto assumed. We have, therefore, in this case too, nothing further to alter than to substitute the above expression for the relative velocity instead of the absolute velocity of the particles which throng into the medium at rest.

This consideration, which Maxwell[1] seems to have employed several times, puts us now in a position to find an expression for the free path not only for a homogeneous gas, but also for the case before us of a molecule of one gas moving in a different gas.

The probable number of collisions experienced by a particle in unit time is equal to the mean number of the other particles which come within the range of its sphere of action during this time as it moves along. The path of the particle in unit time is measured by its velocity, for which, in the case in which all the particles are in motion, we must substitute the expression for the relative velocity just given. While the particle traverses this path its sphere of action moves over a cylindrical path of equal length, the section of which is equal to that of the sphere of action, viz. $\pi\sigma^2$. In this volume, whose magnitude is

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[1] *Phil. Mag.* [4] xix. p. 28; *Scientific Papers*, i. p. 387.

$$\pi\sigma^2\sqrt{(\Omega_1^2 + \Omega_2^2)},$$

there are

$$N_2\pi\sigma^2\sqrt{(\Omega_1^2 + \Omega_2^2)}$$

molecules of the second kind, if $N_2$ denotes the number of these molecules in unit volume; and the number of the collisions that ensue is just the same. If we divide the whole path $\Omega_1$ passed over in unit time by the molecule by this number of collisions, we obtain the mean free path of a particle of the first kind amid a crowd of particles of the second kind for which we are looking, viz.

$$\mathfrak{L}'_1 = \Omega_1 / N_2\pi\sigma^2\sqrt{(\Omega_1^2 + \Omega_2^2)}.$$

In the same way the free path of a molecule of the second kind in a medium consisting of molecules of the first kind is

$$\mathfrak{L}'_2 = \Omega_2 / N_1\pi\sigma^2\sqrt{(\Omega_1^2 + \Omega_2^2)}.$$

In the particular case of the molecules being all of one kind, these expressions turn into the value of the free path already given in § 68 on Maxwell's theory, viz.

$$L = 1 / N\pi s^2\sqrt{2} = \lambda^3 / \pi s^2\sqrt{2};$$

for this assumption gives

$$\Omega_1 = \Omega_2, \quad \sigma = s, \quad N_1 = N_2 = N = \lambda^{-3}.$$

This comparison of the general formula with the special one already known shows the mechanical meaning of the numerical factor $\sqrt{2}$, which was not explained before.

## 97. Molecular Free Path in a Gaseous Mixture

By the help of these formulæ it is now easy to write down the value of the mean free path for the case first mentioned in § 96, where a molecule moves in a mixture of molecules, some of which are of the same and some of a different kind.

If there are $N_1$ particles of the first kind and $N_2$ particles of the second in unit volume, we see at once from the formulæ we have established that the whole number of collisions which a particle of the first gas undergoes in unit time is given by the sum

$$\Gamma_1 \equiv \pi s_1^2 N_1 \Omega_1 \sqrt{2} + \pi\sigma^2 N_2 \sqrt{(\Omega_1^2 + \Omega_2^2)},$$

while

$$\Gamma_2 \equiv \pi s_2^2 N_2 \Omega_2 \sqrt{2} + \pi\sigma^2 N_1 \sqrt{(\Omega_1^2 + \Omega_2^2)}$$

represents the whole number of collisions which a molecule of the second gas experiences in unit time in the mixture.

Hence for the mean free path of a particle of the first kind we obtain the value

$$\mathfrak{L}_1 = \Omega_1 / \Gamma_1,$$

and similarly for a particle of the second gas,

$$\mathfrak{L}_2 = \Omega_2 / \Gamma_2.$$

Both values are dependent on the numbers $N_1$ and $N_2$, and are therefore variable with the ratio of the amounts of the two gaseous components in the mixture.

## 98. Coefficient of Diffusion

If we insert these values of the two free paths $\mathfrak{L}_1$ and $\mathfrak{L}_2$ in the formula of § 95, viz.

$$D = \tfrac{1}{8}\pi(N_1\mathfrak{L}_2\Omega_2 + N_2\mathfrak{L}_1\Omega_1)/N,$$

we obtain the value of the coefficient of diffusion $D$, of which we said in the introductory explanations of § 93 that it possesses the same meaning for the process of diffusion as the conductivity does for the propagation of heat. If this analogy were allowed to be perfect we should expect that, just as the conductivity is a constant magnitude, so too is the coefficient of diffusion, which will always keep the same value in all experiments made with the same pair of gases.

But this expectation is not justified by our formula.[1]

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[1] See also Tait, *Trans. Roy. Soc. Edin.* 1887, xxxiii. p. 266; *Phil. Mag.* [5] xxiii. p. 141.

For by substitution we obtain for the value of the coefficient of diffusion

$$D = \tfrac{1}{8}\pi(N_2\Omega_1^2/\Gamma_1 + N_1\Omega_2^2/\Gamma_2)/N,$$

wherein the magnitudes $\Gamma$ have the meanings

$$\Gamma_1 \equiv \pi s_1^2 N_1 \Omega_1 \sqrt{2} + \pi\sigma^2 N_2 \sqrt{(\Omega_1^2 + \Omega_2^2)}$$
$$\Gamma_2 \equiv \pi s_2^2 N_2 \Omega_2 \sqrt{2} + \pi\sigma^2 N_1 \sqrt{(\Omega_1^2 + \Omega_2^2)}$$

given before. This value is by no means constant; for it depends not only on the temperature by reason of $\Omega_1$ and $\Omega_2$ and on the pressure of the mixture by reason of $N$, but it varies also with $N_1$ and $N_2$, and thus with the ratio in which the two gases have already mixed with each other.

The dependence of the coefficient of diffusion on the temperature and pressure of the gaseous mixture can raise no doubt. The coefficient, however, is to be looked on as a constant in this respect, that it has the same value everywhere throughout the space filled by the gas in an experiment on diffusion, provided that the temperature is kept constant; for the pressure equalises itself everywhere if the diffusion proceeds without a separating partition.

It is also in agreement with experiment if the coefficient of diffusion varies in value with the temperature and total pressure of the gaseous mixture. Loschmidt observed that the value of the coefficient was found to be the greater the higher the temperature in the experiment; and this is shown by the formula too. From the formula also it follows that the value of the coefficient of diffusion alters with the total pressure of the mixture in such wise that $D$ is inversely proportional to this pressure, because the number $N$ of the molecules contained in unit volume varies directly as the pressure. This too is in perfect agreement with Loschmidt's observations.

But our theoretical formula exhibits still another variation of the coefficient of diffusion, which we should not *a priori* expect. The value of $D$ is dependent also on the values of $N_1$ and $N_2$, and these numbers, which express how many molecules of the one or other kind there are in unit volume of the mixture, alter on their side with $x$, as in § 95, and therefore with the position in the tube. The coefficient

$D$ therefore assumes a different value at every different place in the mixture that is being formed by the diffusion; its values consequently alter with the rate of fall of pressure of each of the two gases, so that for the same reason the coefficient is variable with the time during the whole period of the experiment. So the observed values of the coefficient $D$ will not be able to exhibit any perfect agreement together if the observations are made for unequal values of the ratio of mixture $N_1 : N_2$.

The theoretical calculation of an experiment on diffusion therefore becomes very complicated, and so excessively laborious that we easily comprehend why the foregoing formulæ, which were deduced in the first edition of this book, have scarcely at all been used up to now. People have for the most part preferred to employ less exact but more convenient formulæ, which give a constant value for the coefficient of diffusion.

## 99. Another Theory of Diffusion

The theory leads to a constant value of the coefficient of diffusion if a somewhat different fundamental assumption is made as to the cause of the slowness with which the mixture of the two gases proceeds. There can be no doubt but that this cause must be sought in the mutual encounters of the particles, which prevent a forward path in a straight line. But the question may be raised whether the two kinds of molecules take part in these processes in the same way and in equal measure.

It does not seem improbable to assert that the encounters between molecules of the *same* kind have little influence on the velocity of the current with which each of the two gases flows against the other; that just as often as a molecule loses velocity by an encounter with another of the same kind, it happens that it gains velocity in the direction of the flow. Quite otherwise, on the contrary, is the case with encounters between particles of *different* kinds. Since both gases are streaming in different directions, the final result of the encounters between particles of different kinds must be a retardation of the velocities of flow. Hence the cause of the remarkable slowness of the current of diffusion would have to be sought not so much in the obstruction exerted on each other in their flight by particles of the same kind as in the resistance offered by the oppositely moving particles of the other kind met with. It matters, therefore, the less whether, and how often, particles of the same kind encounter each other; it is rather the collisions between molecules of different kinds that have special weight in the determination of the phenomena of diffusion.

These views essentially agree with those which Maxwell[1] and Stefan[2] have placed at the basis of their theories of diffusion, as they assumed a resistance to diffusion which arises from the encounters of the particles of the one gas with the molecules of the other that meet them, while the collisions between particles of the same kind are to remain without influence on the phenomena.

If we adopt this assumption, then, the magnitudes $\mathfrak{L}$ introduced into the formula for the coefficient of diffusion would not really represent the actual free paths of the molecules in the mixture of the two gases; but $\mathfrak{L}_1$ would be the mean value of the path which a particle of the first kind would traverse if it moved solely among particles of the second kind, and likewise $\mathfrak{L}_2$ would be the free path of a particle of the second kind in a medium composed of particles of the first kind only. Hence in the expression for $D$ the values of $\mathfrak{L}'_1$ and $\mathfrak{L}'_2$ deduced in § 96 must be substituted for $\mathfrak{L}_1$ and $\mathfrak{L}_2$.

In this way we should obtain for the coefficient of diffusion the value

$$D = \sqrt{(\Omega_1^2 + \Omega_2^2)}/8N\sigma^2,$$

from which $N_1$ and $N_2$ have disappeared. It has therefore become independent of the ratio of mixture of the two gases, and is therefore to be looked on as *constant*; for it has one and the same value at all points of the tube and at all times during the progress of the experiment. It depends only on the nature of the two diffusing gases, and on the temperature and pressure at which they are; its value also increases as the temperature rises, and it varies inversely as the pressure, just as in the theory first developed and in the observations that Loschmidt has made.

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[1] *Phil. Mag.* 1868 [4] xxxv. p. 199; *Scientific Papers*, ii. p. 57.

[2] *Wien. Sitzungsber.* 1872, lxv. Abth. 2, p. 323.

But this agreement with experiment does not prove the accuracy of the simplified theory. It is still open to the objection that the resistance offered by the other kind of gas is not the only one experienced by a molecule; molecules of the same kind also obstruct a particle in its forward motion, since they, too, can get in its way just like those of the other kind. This resistance of the same medium, and the consequently ensuing shortening of the molecular free path, cannot be left out of account.

The assumption that the current of diffusion of a gas should be resisted only by molecules of the other kind which are moving in the opposite direction rests on a fallacy only. For the velocity of the current is much too little for there to be found in it a sufficient cause why the particles should collide so much oftener or more forcibly with the particles of different kind which meet them than with particles of their own kind, that the influence of the latter should appear vanishingly small.

## 100. Observations in Test of the Theories

Led by these considerations, I spoke out, in the first edition of this book, which appeared in 1877, for the view that the coefficient of diffusion is not constant, but is variable with the ratio of mixture of the gases. But I could not prove the correctness of this assumption, because no decisive experiments had then been made. I could adduce in favour of my conjecture only one observation of Graham's,[1] to which Maxwell[2] had drawn attention; for Maxwell's calculation gave smaller values of the coefficient when the experiment lasted long, and larger values when the period of diffusion was shorter.

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[1] *Brande's Journal*, 1829, pt. 2, p. 74.

[2] *Phil. Mag.* 1868 [4] xxxv. p. 202; *Scientific Papers*, ii. p. 61.

Since this time observations have been made to decide this question, first by Waitz[1] and von Obermayer[2] simultaneously, and somewhat later by Winkelmann.[3] All three observers found that the assumption of a constant value of the coefficient of diffusion of two gases was not sufficient if the experiments were made under varying circumstances.

Waitz, who did not, like his predecessors, chemically analyse the gaseous mixture that resulted at the end of an experiment, but determined its composition by measuring its refractivity during the course of the experiment, was able to determine the value of the coefficient at different places of the diffusion-apparatus at which the mixtures were not alike. He thus obtained, as the means of a number of experiments for three different heights in his apparatus, the values, referred to the centimetre and second,

$$0{\cdot}151, \quad 0{\cdot}154, \quad 0{\cdot}158,$$

for the coefficient of diffusion of carbonic acid into air at 19° C. and under the pressure 751·6 mm. These figures show an increase of the coefficient which is certainly not great, but is still marked, and this increase of the coefficient corresponds to an increase of the amount of carbonic acid in the mixture, which agrees with the theoretical formula. Similar results were obtained by the other observers named, von Obermayer and Winkelmann; their observations, too, confirmed indubitably the fact that the constant of diffusion varies with the ratio of the mixture of the gases.

But when Waitz tried to go into details and to show whether the observed variations of the coefficient conformed numerically to the theoretical formula, a considerable deviation seemed to appear. But it does not at all follow from this that the formula is incorrect; for an objection that is mathematically justified may be raised against the mode of calculation employed by Waitz. With regard to this,

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[1] *Wied. Ann.* 1882, xvii. p. 201; *Inaug. Diss. Berl.* 1882.

[2] *Wien. Sitzungsber.* Abth. 2, 1882, lxxxv. pp. 147, 748; lxxxvii. p. 188.

[3] *Wied. Ann.* 1884, xxii. pp. 1, 152; xxiii. p. 203; 1885, xxvi. p. 105; 1886, xxvii. p. 479.

Hausmaniger[1] has remarked that the formulæ employed by Waitz are founded on the assumption of the constancy of the coefficient of diffusion, and therefore do not apply to the case when it is variable. For the same reason, the conclusions which Winkelmann has drawn from his observations can be maintained only so far as it is shown by them, too, that the coefficient of diffusion, as my theory had predicted, is variable with the ratio of mixture, and therefore also with its rate of fall.

Hausmaniger has therefore taken the trouble to recalculate Waitz's observations by formulæ in which the coefficient of diffusion is taken as variable. But this attempt, too, has unfortunately been unable to obtain agreement between theory and observation; for the measurement of the variability of the coefficient, since it is small, will be made too uncertain by the errors of observation for the law of variation to be established with sufficient exactness.

A comparison of the numbers found by the different observers shows that the uncertainty of the observations is really as large as we say. For the diffusion of carbonic acid into air Loschmidt[2] has found the value of the coefficient, referred to centimetres and seconds, for 0° C. and 760 mm. pressure,

$$D = 0{\cdot}142,$$

while von Obermayer[3] gives

$$D = 0{\cdot}135.$$

These two numbers show as great a difference as the numbers observed by Waitz, which, according to von Obermayer's calculation, assume the values

$$0{\cdot}131, \quad 0{\cdot}133, \quad 0{\cdot}137,$$

when they too are reckoned for the temperature 0° C. and the pressure 760 mm.

We should also on theoretical grounds have been led to expect that the variation of $D$ with the ratio of mixture, determined by the values of $N_1$ and $N_2$, would be quite small. The formula takes the form

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[1] *Wien. Sitzungsber.* 1882, lxxxvi. Abth. 2, p. 1073.

[2] *Ibid.* 1870, lxi. Abth. 2, p. 367; lxii. Abth. 2, p. 468.

[3] *Ibid.* 1880, lxxxi. Abth. 2, p. 1102.

$$D = \frac{\pi}{8N}\left(\frac{\Omega_1^2}{A + B_1 N_1/N_2} + \frac{\Omega_2^2}{A + B_2 N_2/N_1}\right)$$

when for shortness we put

$$A \equiv \pi\sigma^2\sqrt{(\Omega_1^2 + \Omega_2^2)}, \quad B_1 \equiv \pi s_1^2\Omega_1\sqrt{2}, \quad B_2 \equiv \pi s_2^2\Omega_2\sqrt{2},$$

and it then shows that the first of the two terms becomes smaller when the ratio of $N_1$ to $N_2$ increases, but the second becomes larger; the value of $D$ will therefore be able to change with $N_1$ and $N_2$ much less than either of these numbers itself changes.[1]

The alteration of $D$ will be very small when the values of the magnitudes $B$ are nearly equal; and that will occur for the most part. For one of the two gases possesses a greater speed $\Omega$, and a smaller molecular section $\pi s^2$ along with a less molecular weight than the other.

After these considerations and experiments we cannot assert that the theoretical formula for the coefficient of diffusion here obtained has been proved by experiment to be perfectly correct. But it is highly probable from the observations that have hitherto been made that the formula corresponds to the true circumstances. In any case there is no fact known which contradicts it; on the contrary the other formula developed in § 99, which gives a constant value of the coefficient, is certainly inaccurate.

To finally decide as to the validity of our formula we must, as Hausmaniger has already noted, experiment upon gaseous mixtures[2] which contain only small masses of one of the constituents. For when $N_1 = 0$ the formula gives the limiting value

$$D = \Omega_1^2/8N\sigma^2\sqrt{(\Omega_1^2 + \Omega_2^2)},$$

and on the contrary, when $N_2 = 0$, the limiting value

$$D = \Omega_2^2/8N\sigma^2\sqrt{(\Omega_1^2 + \Omega_2^2)},$$

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[1] Guglielmo, *Atti d. Accad. di Torino*, 1882, xvii. p. 106; *Exner's Repert. d. Phys.* 1883, xix. p. 580.

[2] Perhaps by the method recommended by M. Töpler, *Wied. Ann.* 1896, lviii. p. 599.

which are essentially different values [being in the ratio $(\Omega_1/\Omega_2)^2$ or $m_2/m_1$, where $m$ denotes the molecular weight].

But in the conditions that have chiefly been employed in the experiments we can take for the but slightly variable coefficient the value

$$D=\frac{1}{8N}\left\{\frac{\Omega_1{}^2}{\sigma^2\sqrt{(\Omega_1{}^2+\Omega_2{}^2)}+s_1{}^2\Omega_1\sqrt{2}}+\frac{\Omega_2{}^2}{\sigma^2\sqrt{(\Omega_1{}^2+\Omega_2{}^2)}+s_2{}^2\Omega_2\sqrt{2}}\right\},$$

which we find on putting $N_1 = N_2$.

## 101. Dependence on Pressure and Temperature

To test the formula we can also raise the question whether the formula correctly gives the law of dependence of the coefficient of diffusion on both pressure and temperature.

Since both of the mixing gases have the same temperature,

$$m_1\Omega_1{}^2 = m_2\Omega_2{}^2,$$

where $m_1$ and $m_2$ denote the molecular weights of the two gases. If then we denote by $m$ and $\Omega$ the values of the molecular weight and molecular speed for any normal gas which has the same temperature, we have

$$m_1\Omega_1{}^2 = m_2\Omega_2{}^2 = m\Omega^2.$$

By means of this relation the formula for the total pressure

$$p = \tfrac{1}{8}\pi(N_1m_1\Omega_1{}^2 + N_2m_2\Omega_2{}^2)$$

takes the simple form

$$p = \tfrac{1}{8}\pi Nm\Omega^2,$$

wherein $N \equiv N_1 + N_2$ signifies, as before, the total number of all the gaseous molecules of both kinds in unit volume. By this formula we may replace $N$ in the formula for $D$ by the pressure $p$, and we then obtain for the coefficient of diffusion

$$D = \tfrac{1}{64}\pi(m\Omega^2)^{\frac{3}{2}}p^{-1}(\gamma_1{}^{-1} + \gamma_2{}^{-1}),$$

where

$$\gamma_1 \equiv m_1{}^{\frac{1}{2}}\{\sqrt{2}s_1{}^2N_1/N_2 + \sigma^2\sqrt{(1 + m_1/m_2)}\}$$
$$\gamma_2 \equiv m_2{}^{\frac{1}{2}}\{\sqrt{2}s_2{}^2N_2/N_1 + \sigma^2\sqrt{(1 + m_2/m_1)}\}$$

If we put $s_1 = 0 = s_2$, these general formulæ would turn into that which would hold if the mutual collisions of particles of the same kind might be left out of account. We need not therefore pursue this improbable assumption, according to which the coefficient of diffusion would have the constant value

$$D = \frac{\pi(m\Omega^2)^{\frac{3}{2}}}{64\sigma^2 p} \sqrt{\left(\frac{m_1 + m_2}{m_1 m_2}\right)},$$

any further here, if we obtain an answer to our question from the more general formula.

Since the magnitudes denoted by $\gamma$ do not depend on the pressure $p$, the equations show directly that according to the theory *the coefficient of diffusion is inversely proportional to the total pressure of the two diffusing gases.* But this is the very law which Loschmidt deduced in 1870 from his observations, and which has been confirmed by all later experimenters.

Loschmidt has further concluded from his observations that the coefficient of diffusion increases as the temperature rises, and that it increases indeed proportionally to the square of the absolute temperature. The theoretical formula likewise requires an increase of the coefficient with rise of temperature. In the formula $p$ is not variable when we are dealing with experiments that are made at constant temperature and pressure. If the magnitudes $\gamma$ were also independent of the temperature, $D$ would increase proportionally to the $\frac{3}{2}$ power of the absolute temperature (since this on the kinetic theory is proportional to $\Omega^2$), and therefore less than is really the case according to Loschmidt's experiments.

But according to the observations on viscosity the radii $s_1$ and $s_2$ of the spheres of action are dependent on the temperature, either actually or apparently; this is also possible, and, indeed, highly probable, for the newly-introduced magnitude $\sigma$, which has a similar meaning. If we may assume that $\sigma$ and the magnitudes $s$ are variable, at least approximately, in the same way with the temperature, the coefficient of diffusion $D$ must increase with the temperature, according to the same law as the product of the coefficient of viscosity $\eta$, which, according to § 78, is given by the formula

$$\eta = 0{\cdot}30967\ m\Omega/\pi s^2\sqrt{2},$$

into the absolute temperature or the magnitude $1 + a\vartheta$, where $\vartheta$ is the centigrade temperature and $a$ is the coefficient of expansion.

Now, the value of the coefficient of viscosity, according to the observations described in § 85, increases with the temperature in such wise that it may be taken, at least approximately, to be proportional to the function

$$(1+a\vartheta)^n,$$

where the exponent $n$ has values which for different gases lie between 0·75 and 1; its value being greater for the easily condensible gases than for those which were formerly considered permanent. We should have then to expect that the coefficient of diffusion varies as

$$(1+a\vartheta)^{1+n},$$

where $n$ has the value appropriate to the gas.

The observations from which Loschmidt[1] has concluded the law put forward by him were made with three pairs of gases diffusing into each other, viz. carbonic acid and air, carbonic acid and hydrogen, hydrogen and oxygen. The value of $n$ for carbonic acid, which occurs in the first two pairs, has been found, from experiments on viscosity, to be nearly equal to 1, so that Loschmidt's observations on the diffusion of this gas are in excellent agreement with the investigations of the viscosity of the same gas. For hydrogen and oxygen the value of $n$ given by the experiments on viscosity is certainly less; but the agreement in Loschmidt's experiments on diffusion is not so great that we are forced to assume the exponent $n$ to be always exactly equal to 1.

In fact von Obermayer[2] found later, by experiments on diffusion, that the exponent has different values for different gases, and his observations give for

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[1] *Wien. Sitzungsber.* 1870, lxi. Abth. 2, p. 367; lxii. Abth. 2, p. 468.

[2] *Ibid.* 1880, lxxxi. Abth. 2, p. 1102.

| | |
|---|---|
| Air—carbonic acid | $n = 0{\cdot}968$ |
| Hydrogen—oxygen | 0·755 |
| Carbonic acid—nitrous oxide | 1·050 |
| Carbonic acid—hydrogen | 0·742 |
| Oxygen—nitrogen | 0·792 |

and these values so far agree with those which the same observer[1] obtained for the dependence of the coefficient of viscosity on the temperature, viz.

| | |
|---|---|
| Air | $n = 0{\cdot}76$ |
| Hydrogen | 0·70 |
| Oxygen | 0·80 |
| Nitrogen | 0·74 |
| Nitrous oxide | 0·93 |
| Carbonic acid | 0·98 |

that the exponent for the diffusion in the case of any pair lies, with one exception, between the exponents for the viscosity of the two gases concerned.

From these experiments we cannot doubt that the variability of the two phenomena, viscosity and diffusion, with the temperature is to be referred to exactly the same causes. Both coefficients, that of viscosity and that of diffusion, depend on the temperature, not only because their formulæ contain the molecular speed $\Omega$, but also in so far as the radii $s$ and $\sigma$ of the spheres of action are variable with the temperature. The only difference in their variability with the temperature consists in that for diffusion being greater than that for viscosity in the ratio of $1 + a\vartheta$ to 1.

We may further conclude that the change of both magnitudes $s$ and $\sigma$ with the temperature is effected by forces that are equal or, at least, of like kind. Both magnitudes are radii of spheres of action; $s$ refers to the mutual action of similar molecules, while $\sigma$ denotes the distance apart of dissimilar molecules when they collide and, therefore, the radius of this sphere for the action of dissimilar particles on each other. If, now, as we saw in our discussion of viscosity, the diminution of the radius $s$ of the sphere of action with rise of temperature is only apparent, and is to be referred to forces of cohesion, as with Sutherland's explanation, we shall have to assume, in the same way, that the magnitude $\sigma$ also appears to diminish with rise of temperature only because the forces of cohesion, or, more accurately, the attractive forces exerted by dissimilar molecules on each other, heighten the probability of an encounter, and, indeed, increase it the more strongly the less the speed $\Omega$ of the molecular motion or the lower the temperature. Accordingly the law of dependence of the coefficient of diffusion on the temperature must be represented by a formula which must be formed quite similarly to that found for viscosity (§ 85), viz.

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[1] *Wien. Sitzungsber.* 1876, lxxiii. Abth. 2, p. 433; Carl's *Repert.* 1877, xiii. p. 130. Compare § 85.

$$\eta = \eta_0(1 + a\vartheta)^{\frac{1}{2}}(1 + aC)/(1 + C/\Theta);$$

we shall therefore have to put

$$D = D_0(1 + a\vartheta)^{\frac{3}{2}}(1 + aC')/(1 + C'/\Theta),$$

where $a$ represents the coefficient of expansion, and $\Theta$ the absolute temperature

$$\Theta = \vartheta + a^{-1} = \vartheta + 272{\cdot}5,$$

while $D_0$ stands for the value of $D$ at 0° C., and $C'$ is a constant which represents the measure of the cohesion between dissimilar particles, as does $C$ for similar particles.

We may omit a detailed comparison of this theoretical formula with the observations; for, since Sutherland's formula has been proved for viscosity, the agreement of the values of the exponent $n$ now shows that the formula for the diffusion can represent the results of experiment in the same excellent way. It is therefore sufficient to give the values of $C'$ which Sutherland[1] has calculated from von Obermayer's experiments on diffusion:—

| | |
|---|---|
| Carbonic acid—air | $C' = 250$ |
| Carbonic acid—hydrogen | 106 |
| Carbonic acid—nitrous oxide | 380 |
| Oxygen—hydrogen | 100 |
| Oxygen—nitrogen | 136 |
| Oxygen—carbon monoxide | 124 |

As we should expect, these values correspond in magnitude to those which Sutherland has calculated for the simple gases from the observations on viscosity (§ 85).

In the same memoir Sutherland also submits to calculation, in accordance with his theory, the observations which Winkelmann has made on the diffusion of vapours into gases. The same vapours which Lothar Meyer, Schumann, and Steudel had employed for their experiments on transpiration (§ 86) served also in these experiments. Here also the agreement between the calculations from both series of experiments is satisfactory.

## 102. Calculation of the Coefficient of Diffusion from the Coefficient of Viscosity

The agreement between the measurements of the viscosity and diffusion goes still further. In the first memoir he published on this theory Maxwell[2] had already deduced from observations on diffusion a value of the free path of gaseous molecules, which harmonises well with the value determined for air from experiments on viscosity. But the connection into which these two different phenomena are brought by the kinetic theory came more strikingly into view when Stefan[3] calculated the numerical values of the coefficients of diffusion directly from the coefficients of viscosity, and thereby found numbers which agreed quite well with Loschmidt's experiments.

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[1] *Phil. Mag.* 1894 [5] xxxviii. p. 1.

[2] *Ibid.* 1860 [4] xx. p. 21; *Scient. Papers*, i. p. 392.

[3] *Wien. Sitzungsber.* 1872, lxv. Abth. 2, p. 323.

The possibility of such a calculation from our formulæ is at once evident when we remember that the absolute values of the free paths

$$L_1 = \lambda^3/\pi s_1{}^2\sqrt{2}, \quad L_2 = \lambda^3/\pi s_2{}^2\sqrt{2},$$

of each of the two diffusing gases in an unmixed state, in which they are under the normal pressure $p$ and contain $N$ molecules in unit volume, can be calculated from the coefficient of viscosity, and that therefore the magnitudes

$$N\pi s_1{}^2\sqrt{2} = L_1{}^{-1}, \quad N\pi s_2{}^2\sqrt{2} = L_2{}^{-1}$$

are known. Stefan used further the hypothesis already mentioned in § 96, viz.

$$\sigma = \tfrac{1}{2}(s_1 + s_2),$$

which allows us to evaluate the magnitude

$$N\pi\sigma^2 = (L_1{}^{-\frac{1}{2}} + L_2{}^{-\frac{1}{2}})^2/4\sqrt{2}.$$

Since also the molecular speeds $\Omega$ are known, we have all the magnitudes given which come into the formula for the coefficient of diffusion, and the value of this coefficient, therefore, can be calculated in absolute measure if the coefficient of viscosity is measured for each of the two gases that take part in the diffusion.

Stefan has carried out this calculation for the gases the diffusion of which has been experimentally investigated by Loschmidt, and has arrived at a tolerably good agreement between the theoretically calculated numerical values and those deduced from the observations. But since he made his calculation from another formula, I have had to repeat the calculation.

Since Loschmidt has always in his experiments allowed equal volumes of the two diffusing gases to mix together, I have put the numbers $N_1$ and $N_2$ equal to each other, and so have made my calculation by the formula that is given at the end of § 100. The values of the molecular free paths and speeds that are introduced are those we have given before; the values, however, at 0° C. are not used directly, but are reduced to the temperature of Loschmidt's experiments. In the following table the values so calculated are tabulated together with those observed, the centimetre and second being taken as units :—

*Coefficients of Diffusion.*

| | Calculated | Observed |
|---|---|---|
| Hydrogen—oxygen . . . . . | 0·688 | 0·722 |
| Hydrogen—carbon monoxide . . | 665 | 642 |
| Hydrogen—carbonic acid . . | 575 | 556 |
| Hydrogen—sulphurous acid . . | 499 | 480 |
| Carbon monoxide—oxygen . . | 174 | 180 |
| Oxygen—carbonic acid . . . | 133 | 161 |
| Carbon monoxide—carbonic acid . | 133 | 160 |
| Marsh gas—carbonic acid . . | 139 | 159 |
| Air—carbonic acid . . . . | 133 | 142 |
| Nitrous oxide—carbonic acid . . | 097 | 089 |

The agreement of the theory with experiment is of course not entirely perfect, but is sufficiently good for us to see in it a further important argument for the correctness of the hypotheses of the kinetic theory. For it remains, indeed, a striking and remarkable circumstance that the coefficient of diffusion may be calculated from that of viscosity with so near an approximation.

The differences that yet remain between the calculated and observed numbers may be explained on different grounds. It seems to me most probable that Stefan's hypothesis of the simple relation

$$\sigma = \tfrac{1}{2}(s_1 + s_2)$$

between the radii of the different spheres of action does not hold with accuracy. For the forces between similar molecules on the one hand and dissimilar molecules on the other may have very different intensities, and there perhaps exists a different relation between the shortest distances to which two molecules can approach each other.

A second ground for the want of agreement undoubtedly resides in the accumulation of the errors of the manifold data of experiment employed one after another, which are all combined in the result and may give rise to great uncertainty. The values of the molecular speeds have been calculated from the observed densities, the free paths from the coefficients of viscosity. Lastly, we have also used the molecular weights and, therefore, stoichiometrical measures. Consequently, at least six different observations, of which each is affected with an error, are employed for each of the calculated values of the coefficients of diffusion.

In addition to these grounds, which are indeed sufficient of themselves, defects in the theory may have contributed to the discrepancies, since the theory of diffusion has not been carried out with such strict mathematical accuracy as was the theory of viscosity. That a more accurate calculation would improve the agreement seems to me the more probable as my figures fit in with the observations better than those of Stefan, which were calculated from a formula that leads to a constant value of the coefficient of diffusion.

Now that this relation between the viscosity and diffusion of gases is known, we seem to be fully justified in applying the observations on diffusion, in the same way as those on viscosity, to extend our knowledge of the direct properties of the molecules, and indeed first to calculate the molecular free path. Observations on viscosity certainly deserve to be preferred for this purpose, in so far as the processes of friction are more easily and simply treated theoretically. But when there is a question as to the magnitudes of $s$ and $\sigma$, diffusion-experiments are the best means of teaching us something about $\sigma$. Von Obermayer[1] has employed his observations on diffusion for purposes of this kind. He thereby obtained for the sections of the spheres of actions numerical values[2] which are about $1\frac{1}{2}$ times greater than those calculated[3] by me from the viscosity; but the reason of this simply resides in his having employed a formula for his calculation which leads to a constant value of the coefficient of diffusion; he neglects, therefore, the resistance which the molecules of the same kind offer to each other, and therefore finds the resistance of the dissimilar molecules too large, and so estimates the section of the sphere of action $\pi\sigma^2$ also too large. He thus arrives at results whose lack of agreement with experiment must be taken as a proof that the formulæ which give a constant value for the coefficient of diffusion are inexact.

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[1] 'Experiments on Diffusion, III.' *Wien. Sitzungsber.* 1883, lxxxvii. Abth. 2, p. 188.

[2] See p. 197 of the memoir cited.

[3] Compare Chapter X.

# CHAPTER IX

## *CONDUCTION OF HEAT*

### 103. Low Conductivity of Gases

Only very little was known respecting the conduction of heat in gases before the development of the kinetic theory of heat. The experiments made by Andrews,[1] Magnus,[2] and Péclet[3] show nothing more than that heat is propagated in gaseous media not only by radiation, but also by conduction as in solid and liquid bodies; but the experiments gave no measurements of the conductivity of gases, and only showed that it is very much less than the conductivity of solids and liquids. Among the gases hydrogen is distinguished, as was long ago known to Priestley[4] and Achard,[5] by so considerably greater a conductivity that Magnus thought it might be compared with that of metals; however, later observations have shown it to be something like 1,000 times less than that.

The vapours also of liquids, just like the real gases, have only a small capacity for conducting heat. The most striking proof of this fact is furnished by Leidenfrost's[6] experiment with a drop of water on a hot plate, as it shows that the layer of vapour which is formed between the drop and the plate prevents the passage of heat to such an extent that the water does not reach boiling-point.

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[1] *Proc. Irish Acad.* 1841, i. p. 465; Berzelius' *Jahresb.* xxii. p. 24.

[2] *Pogg. Ann.* 1861, cxii. p. 497.

[3] *Traité de la Chaleur*, 3rd ed. 1861, iii. p. 418.

[4] *Experiments and Observations relating to Various Branches of Natural Philosophy*, Birmingham 1781, i. sect. 33, § 5, p. 378.

[5] *Mém. de l'Acad. de Berlin*, Année 1783, p. 84, Berlin 1785.

[6] Leidenfrost, *De aquæ communis nonnullis qualitatibus tractatus*, § 51, Duisburgi 1756. *Opuscula phys.-chem. et med.* iii., Duisburgi 1797.

At the time when Clausius laid the foundation of the kinetic theory the low conductivity of gases and vapours was adduced, as has been already mentioned in § 61 at the beginning of Part II., as the most weighty objection to the correctness of the new hypothesis. It was asserted that in a medium the molecules of which are moving with great speed the heat, which consists in the energy of motion of the molecules, must also be transferred with similar speed from one spot to another. This objection we may still attempt to maintain, even if the similar objection which has been raised in respect to the diffusion of gases is already removed. For although it has been shown that on this theory the mixing of two gases does not proceed with the speed at which the molecules move, but very slowly, because the molecules frequently collide and therefore traverse only very short distances in spite of their large speed, yet this answer to the doubts derived from the phenomenon of diffusion cannot without more consideration be applied to the phenomenon of conduction, since in diffusion there is a question of a transference of mass, and in conduction, on the contrary, of a transference of energy.

This difference is best illustrated by an example which seems to lead to a conclusion by analogy. A very common piece of physical apparatus consists of a row of elastic balls which hang in contact and are used for experiments on the collision of balls. If, for instance, we allow one of these balls to fall against the remainder of the row, it comes to rest itself on the collision if all the balls are of the same size, and all the others remain at rest except the last, which flies off from the rest with the same speed with which the first struck the row. In this experiment the energy alone of the motion has been propagated, and, indeed, with very great speed, without the mass through which the transmission was effected—that is, the row of intermediate balls—being carried on with the energy. We might likewise conclude that the energy of the heat-motion may be very rapidly transmitted by means of a group of molecules, which now and then collide and mutually transmit energy to each other in the collisions, without the molecules which effect the transmission having themselves to move in the direction of the motion of the heat.

But this instance in illustration of the objections contains in itself its own refutation, for it does not correspond in all points to actuality. In the collision-apparatus the transmission of energy takes place at all the collisions in the same direction, and travels therefore over a wide stretch in a short time. But in the gaseous medium in which the molecules collide now in this direction and now in that, the energy is carried over now here and now there, and is jerked about in the same zigzags as the molecules. The transmission of heat therefore goes on in a fixed direction with slowness similar to that of the forward motion of the molecules.

## 104. Kinetic Theory of Conduction

Starting from this conception Clausius,[1] a short time after Maxwell,[2] who first treated the problem, gave a detailed analysis of the process of the conduction of heat, by which he has removed the last doubts before mentioned regarding his hypothesis. Stefan[3] and von Lang[4] have later given elementary demonstrations of this theory. The same question has been mathematically treated by Boltzmann[5] on the basis of a later hypothesis of Maxwell's, according to which the molecules of gases repel each other with forces that are inversely as the fifth power of the distance. The theory given in the Mathematical Appendices of this book starts from Maxwell's older view and rests on Maxwell's law of distribution of speeds.

[1] *Pogg. Ann.* 1862, cxv. p. 1; *Abhandl. ü. Wärmetheorie*, 1867, Abth. 2, p. 277; *Mechanische Wärmetheorie*, iii. p. 105.

[2] *Phil. Mag.* 1860 [4] xx. p. 31; 1868, xxxv. p. 214. *Scient. Papers*, i. p. 403; ii. p. 74.

[3] *Wien. Sitzungsber.* 1863, xlvii. Abth. 2, p. 81.

[4] *Ibid.* Abth. 2, 1871, lxiv. p. 485; 1872, lxv. p. 415; *Pogg. Ann.* 1871, cxlv. p. 290; 1872, cxlviii. p. 157; *Einleitung in die theor. Physik*, 1867, p. 529.

[5] *Wien. Sitzungsber.* 1872, lxvi. Abth. 2, p. 330; 1875, lxxii. Abth. 2, p. 458.

It is easy to give an idea of the matter contained in these mathematical theories without repetition of the calculation, because the analogy of the problem before us with the theories earlier discussed is obvious. Diffusion consists in a transference of *mass* effected by means of the molecular motions and viscosity in a transfer of forward *momentum* caused by the same means; conduction of heat is likewise a transfer of *energy*, which is effected as before by the motion of the molecules. This similarity goes so far that the propagation of heat may be directly looked on as a diffusion-phenomenon in which the warmer and colder particles diffuse among each other. For, since the molecules as they pass from an upper and warmer layer to a lower and colder one retain their energy till a collision, the process of conduction of heat is completely identical with that of diffusion; and we have no further difference to take into account than this, that we have now to find, not the number of the diffusing particles, but the sum of their energy.

In order to form a distinct idea of the arrangement of the experiment that shall correspond as nearly as possible to that chosen before, let us consider a gas enclosed between two unlimited, or, at least, very widely extending, parallel plane walls which lie horizontally with the distance between them equal to the unit of length; and consider the lower to be kept at the constant temperature 0° C., and the upper at the temperature 1° C. Under these circumstances a distribution of temperature is produced of itself between the walls which is independent of the time, and such that at the height $x$ above the lower limiting plane the temperature is

$$\vartheta = x.$$

A constant flow of heat in the direction from above to below takes place in the gas, and this is such that through each imaginary horizontal plane in the space occupied by the gas there flows an equal amount of heat in unit time. In accordance with the usual definition we denote as *the coefficient of conductivity* of the gas [or simply its *conductivity*] that amount of heat which in unit time passes through unit area of such a horizontal plane under the given circumstances.

If we now go back to the consideration respecting the current of diffusion which was worked out in § 95, we have merely to change the meaning of the symbol $n$ which occurs in it in order to apply it to the flow of heat. There $n$ denoted the difference of the values which the number of molecules per unit volume of one of the two diffusing gases has in two different layers separated by unit length. We may take over this signification to the present problem in so far as we can refer it to the number of warmer or colder particles which meet each other; we understand therefore by $n$ the difference of the values of the number of the, for instance, warmer particles in two different layers which are separated by unit of length. Then it follows that the number of particles which in unit time carry heat over unit area may be expressed by the product

$$nD,$$

where $D$ denotes the coefficient of diffusion.

We have, however, yet another alteration to consider; for we have no longer to do with the number of particles that pass across, but, as we have already said, with the energy carried over by them. Instead, therefore, of the number $n$, we must introduce the difference of the heat-energy per unit volume at two layers which are distant from each other by unit length.

We have taken the difference of temperature corresponding to this distance to be 1 degree; hence the difference in the thermal energy of a molecule in two layers separated by unit length is $mc$ calories, if $c$ denotes the specific heat at constant volume and $m$ the mass of a molecule. It thus follows that the difference of the energies per unit volume for which we are looking is

$$Nmc$$

in thermal units, if $N$ denotes, as before, the number of molecules in unit volume, and the expression

$$\mathfrak{k} \equiv NmcD$$

results on our theory for the quantity of heat which is termed the *coefficient of conductivity*.

The coefficient of diffusion $D$, which was determined in § 95 by the formula

$$D = \tfrac{1}{8}\pi(N_2\mathfrak{L}_1\Omega_1 + N_1\mathfrak{L}_2\Omega_2)/N,$$

becomes

$$D = \tfrac{1}{8}\pi\Omega L$$

in our special case in which the two kinds of gas are the same, for we may neglect the small difference in the values of $\Omega$ and $\mathfrak{L}$ that arise from the inequality of temperature, and therefore by §§ 96 and 97 put

$$\Omega_1 = \Omega_2 = \Omega, \quad \mathfrak{L}_1 = \mathfrak{L}_2 = L\,;$$

and by § 95 we have also

$$N_1 + N_2 = N.$$

The conductivity of a homogeneous gas for heat is therefore

$$\mathfrak{k} = \tfrac{1}{8}\pi Nm\Omega Lc.$$

## 105. Relation of the Conduction of Heat to the Viscosity

The formula shows a simple relation of the conductivity to the coefficient of viscosity which by § 78 is given by the formula

$$\eta = 0{\cdot}30967\ Nm\Omega L.$$

From this we find that the conductivity can be expressed in terms of the viscosity and the specific heat of the gas as in the equation

$$\begin{aligned}\mathfrak{k} &= (\tfrac{1}{8}\pi/0{\cdot}30967)\ \eta c\\ &= 1{\cdot}26812\ \eta c.\end{aligned}$$

The factor which occurs in this formula is not much greater than 1, and we should not be unjustified if in this theory, which depends only on approximation, we were to put it equal to 1, and thus obtain

$$\mathfrak{k} = \eta c.$$

This value would, indeed, have directly resulted if we had used the formula for the coefficient of viscosity as given by Stefan,[1] viz.:—

$$\eta = \tfrac{1}{8}\pi Nm\Omega L,$$

which, if we are contented with a somewhat less accuracy, seems quite justified, and is therefore mentioned frequently in memoirs. The reason that we have arrived at different values of the numerical coefficients in our formulæ for $D$ and $\eta$, viz. $\frac{1}{8}\pi \equiv 0{\cdot}39270$ and $0{\cdot}30967$, is that in the calculation of $\eta$ a higher degree of approximation has been aimed at and attained.

We have already met with a similar uncertainty of the numerical factors that come into formulæ; it is in all cases caused by the different way in which the mean is taken of the varying properties and circumstances of the molecules. In an elementary theory it is not, indeed, possible to keep up the consideration of all conceivable particular cases right on to the end through the whole calculation, and then at the conclusion—and not till then if we are to be accurate—to form the sum and take the mean. We are obliged, on the contrary, for greater simplicity and clearness of procedure, not only to deduce the mean result for each part of the calculation by itself, but also to employ from the first average values of the magnitudes that come into the calculation instead of the real ones. Since the concluding result of such a calculation can be only approximate, we must not be surprised that the theories given by different investigators have led to different values of the numerical coefficients. All, however, agree in concluding that the conductivity $\mathfrak{k}$ and coefficient of viscosity $\eta$ are connected by the relation

$$\mathfrak{k} = \kappa\eta c,$$

where $c$ is the specific heat of the gas at constant volume, and $\kappa$ a numerical coefficient which has the same value for all gases. This value lies between 0·5 and 2·5.

In § 57* of the Mathematical Appendices to this work I have given a calculation in which I have striven to find the value of the coefficient $\kappa$ as exactly as possible. This calculation, in which the mean values have been taken with due regard to Maxwell's law of distribution of speeds, has given

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[1] *Wien. Sitzungsber.* 1872, lxv. Abth. 2, p. 363. Compare § 48* in the Mathematical Appendices.

$$\mathfrak{k} = 1{\cdot}6027\ \eta c.$$

If we compare the mathematical calculation which has led to this larger value of the coefficient $\kappa$ with that here deduced in an elementary way, the difference will perhaps astonish us, and give rise to the objection that in laying down the mathematical formula we have taken into account the kinetic energy of the molecular motion only, while at the end we have substituted for this kinetic energy simply the specific heat at constant volume $c$ multiplied by the absolute temperature. This procedure seems to contradict the view as to the ratio of the molecular energy to the total energy which is put forward in § 53; for it is there proved that the kinetic energy of the rectilinear motion of the molecules of a gas forms only a part of the whole energy contained in the gas. We might therefore be inclined to assume that the calculation in which account is taken only of the energy of the molecular motion will give a result, the validity of which should be limited to the propagation of that energy only; and that we should therefore consider the value 1·6027 of the coefficient $\kappa$ to apply only to the propagation of the molecular energy; and we might consider it possible that the remainder of the energy forming the heat of the gas, and therefore the energy of the motions which the individual particles execute within the molecules and the whole potential energy, may be propagated with a different speed, either smaller or larger, than that of the kinetic energy.

In fact, the assumption has many times been made, especially by Stefan[1] and Boltzmann,[2] that the kinetic energy of the molecular motion is passed on from place to place with greater speed than the remaining energy, which in Chapter V. we have termed the atomic energy. We were at that time obliged to yield to this view, because no other possibility was seen of bringing the theoretical law

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[1] *Wien. Sitzungsber.* 1875, lxxii. Abth. 2, pp. 74, 75.

[2] *Ibid.* p. 458; *Pogg. Ann.* 1876, clvii. p. 457.

$$\mathfrak{f} = \kappa \eta c$$

into a complete agreement with the observations then published. It had, in fact, been apparently established that a smaller value must be assigned to the factor $\kappa$ for gases whose atomic energy forms the greater part of the whole energy than for the other gases in which the molecular energy exceeds the atomic energy. These facts would really be very simply explained on the hypothesis named, according to which the gases with preponderating molecular energy must have a better conductivity than the other gases with greater atomic energy and smaller molecular energy.

Theoretical reasons could also be adduced for this hypothesis which at that time seemed to be unavoidably necessary from the results of the experimental measures that had been made. If we consider the processes that occur during the encounter of complicated molecular structures, we may become inclined to the view that the motion of both centres of gravity will chiefly be altered by the collision, while many parts of each complex of atoms may scarcely be disturbed in their own motions. The molecular energy would therefore be carried over from place to place with greater speed or in a higher degree, or, in other words, the conductivity of the gases would be greater for the molecular energy than for the atomic energy.

In the first edition of this book, which was published in 1877, I explained these ideas as possible and admissible because I knew no better explanation of the facts, although even at that time I raised several weighty objections to them. At the same time, however, I pointed to another interpretation, in expressing my belief that all differences between theory and observation might find their explanation in the accumulation of the errors of experiment.

The most important objection that can be urged against this hypothesis, that gases have unequal conductivities for their molecular and atomic energy, is that it contradicts an important fundamental theorem of the kinetic theory. As has been mentioned in § 53, Clausius has established the proposition that in a perfect gas the kinetic energy of the molecules bears an always constant ratio to the whole energy contained in the gas; and this theoretical proposition is experimentally confirmed by the experiments that have been made for the measurement of the specific heats. If now a greater amount of molecular energy were brought to a point in a gas in consequence of the assumed better conductivity for it, the necessary consequence would, according to this proposition of Clausius, be that a compensation would at once result by the atomic energy gaining at the expense of the molecular until the proper ratio was again restored. By this the untenability of that hypothesis might be established, at least for perfect gases.

Now, there are certainly many gases and vapours for which Clausius' proposition cannot hold in all strictness, because their specific heats are not constant, but are highly variable with the temperature. For such cases a different consideration would be in place, which rests on the proposition of the conservation of energy alone. According to this law the discussion of considerations respecting the conditions during an encounter has no bearing on the resolution of our doubt. If a particle has flown from one place to another, it has carried over with it to its new place the whole amount of its energy—not its kinetic energy only, but also the whole of its internal or atomic energy—and it is an entirely unimportant question whether and how this energy is transformed by the collisions that afterwards occur.

Hence it follows that the conductivity of a gas for every kind of energy is the same, and that if the formula

$$\mathfrak{k} = 1{\cdot}6027\,\eta c$$

holds for the conduction of the molecular kinetic energy, it must also hold for the conduction of heat generally.

## 106. Theoretical Laws of the Conduction of Heat

The conclusion of the theory which we have found requires the conductivity of a gas for heat to obey the laws which hold for the coefficient of viscosity and for the specific heat.

The kinetic theory of gases has led to the discovery, which has afterwards been confirmed by experiment, that the coefficient of viscosity of a gas is independent of its pressure or density. It also follows from this theory that the same value must be found for the specific heat at constant volume, referred to unit mass of the gas, if the experiment is made with a different volume or at a different pressure; for the number of molecules of a gas which are contained in unit mass of the gas require under all circumstances the same addition of energy when this mass is warmed by 1 degree without expanding, and therefore without doing work. In agreement with this theoretical result the experiments of Regnault[1] have shown that the specific heats of air, hydrogen, and carbonic acid, measured at constant volume, are independent of the pressure.

Since, then, not only the coefficient of viscosity, but also the specific heat, is independent of the pressure of the gas, the theory leads to the law laid down by Maxwell and by Clausius that *the heat-conductivity also of a gas for heat is not variable with its pressure.*

Regnault has further found that the specific heat of chemically simple gases is independent also of the temperature. Probably all gases whose molecules are composed of only two atoms have this property, to judge from E. Wiedemann's[2] observations. On the kinetic theory, therefore, *the heat-conductivity of a diatomic gas increases with the temperature according to the same law as its coefficient of viscosity.*

The laws we have cited for the specific heat do not, however, hold without limitation. The more easily condensible gases and vapours do not obey these laws, at least in all strictness. Hence, also, the theoretical laws of the conduction of heat deduced from these empirical rules cannot be extended without objection to vapours, nor to condensible gases, nor to gases of complicated chemical structure; for these media the laws have only an approximate applicability.

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[1] *Mém. de l'Acad. de Paris*, 1862, xxvi.

[2] *Pogg. Ann.* 1876, clix. p. 1.

## 107. Observations of the Conductivity at Different Pressures

That the heat-conductivity of gases is really independent of the pressure, as the theory requires, has been shown by Stefan's[1] experiments, in which a measurement of the conductivity of gases was given for the first time in absolute measure.

After he had convinced himself by preliminary experiments that the method followed by Magnus is unsuitable for the purpose, by reason of the simultaneous conduction of heat through the walls of the gasholder,[2] Stefan employed Dulong and Petit's method, which had shortly before been also used by Narr[3] in comparative experiments on the speed of cooling in different gases. In a cylindrical chamber fitted with the gas under investigation was a similar cylindrical holder, which was filled with air or other gas, and provided with a manometer, whereby it was ready to serve as an air-thermometer. Stefan made observations with this apparatus by immersing it, when initially at the temperature of the room, in melting snow, and measuring the speed of cooling of the air-thermometer by observation of the falling condition of the manometer.

It is by this method, or by similar methods which have been partly improved, that most of the later measures of the heat-conductivity of gases have been made. In addition to a second memoir by Stefan[4] and two investigations by Josef Plank on gaseous mixtures[5] and a few pure gases[6] which are a continuation of it, several more valuable memoirs have been published by Winkelmann,[1] Kundt and Warburg,[2] Janssen,[3] Graetz,[4] Eichhorn,[5] and others. Schleiermacher[6] made his observations by Andrews' method.

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[1] *Wien. Sitzungsber.* 1872, lxv. Abth. 2, p. 45.

[2] Buff has confirmed this. *Pogg. Ann.* 1876, clviii. p. 177.

[3] *Ibid.* 1871, cxlii. p. 123.

[4] *Wien. Sitzungsber.* 1875, lxxii. Abth. 2, p. 69.

[5] *Ibid.* 1875, lxxii. Abth. 2, p. 269.

[6] *Ibid.* 1876, lxxiii. Abth. 2, p. 123; *Carl's Repert.* 1877, xiii. p. 164.

I first bring forward some of Stefan's results for the experimental proof of the theoretical law that the conductivity of a gas is independent of its pressure. From four observations on air under the ordinary pressure of about 750 mm. of mercury Stefan found the following values, referred to the centimetre and second as units, for $10^7\mathfrak{k}$, viz. 554, 560, 552, 554, and thus the mean value

$$\mathfrak{k} = 0{\cdot}0000555\,;$$

and when he rarefied the air to the pressure 428 mm. he found in the same way $\mathfrak{k} = 0{\cdot}0000552$.

If, then, there is a diminution of the conductivity with the density, this is certainly so small as to elude observation.

Kundt and Warburg obtained similar results by observing the cooling of a mercury thermometer in a closed space. They found the following values for the interval $t$ which was necessary for the thermometer to cool from 59·3° C. to 19·6° C. when the apparatus was filled with the gases named at the pressures specified.

| | | |
|---|---|---|
| Air . . . | $p =$ 19·5 mm. | $t =$ 277 secs. |
| | 9 | 277 |
| | 4 | 278 |
| | 0·5 | 280 |
| Carbonic acid . | $p =$ 7·7 | $t =$ 349 |
| | 1·5 | 350 |
| Hydrogen . . | $p =$ 154 | $t =$ 66 |
| | 8·8 | 68 |

The constancy of the conduction and radiation of heat comes out plainly from these numbers, at least within the given limits of the pressure. Under greater pressure the regularity was disturbed by currents of the gas.

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[1] *Pogg. Ann.* 1875, clvi. p. 497; 1876, clvii. p. 497; 1876, clix. p. 177; *Wied. Ann.* 1877, i. p. 63; 1880, xi. p. 474; 1883, xix. p. 649; 1886, xxix. p. 68; 1891, xliv. p. 177; 1893, xlviii. p. 180.

[2] *Pogg. Ann.* 1875, clvi. p. 177; previously in abstract in *Berl. Monatsber.* 1875, p. 160.

[3] *Wied. Beibl.* 1879, iii. p. 701.

[4] *Wied. Ann.* 1881, xiv. p. 232; *Münch. Habilitationsschrift*, 1881.

[5] *Ibid.* 1890, xl. p. 697.

[6] *Ibid.* 1888, xxxiv. p. 623; 1889, xxxvi. p. 346.

In the opposite case also, when the pressure was made very small, Kundt and Warburg observed deviations from constancy; there is here, however, no question of currents in the gas but of a phenomenon of a similar kind to that noticed by them in their experiments on viscosity, which have been described in § 81. Just as the slip of a gas on the wall of the containing vessel becomes the more appreciable the further the rarefaction is carried, so a difference between the temperature of the enclosure and that of the gas touching it becomes the more considerable the less the pressure. If the pressure is high and the gas dense, many particles strike against the wall and cause so complete an interchange of heat that only a small difference between their temperatures can arise. But if the pressure becomes smaller, and therefore the number of particles fewer, the difference of temperature increases and may become so great as to amount to several degrees.

This behaviour is quite analogous to that observed in connection with viscosity; for in viscosity the internal friction alone comes into account in dense gases, while in rarefied gases the phenomenon depends, not only on the internal friction, but also on the external friction as well; and, just in the same way, the conduction of heat in dense gases practically depends only on the internal conductivity of the gas, while in rarefied gases it is conditioned by the external conductivity as well. The internal conductivity, like the internal friction, is independent of the density and pressure; the external conductivity, however, alters, like the external friction, with the pressure, and, indeed, according to the same law. In both cases there is a simple proportionality to the pressure, and for the same reason in both cases; for both the external friction and the external conduction increase in the ratio of the number of the particles which meet the wall.

For the clear recognition of this behaviour, first noted by Kundt and Warburg, the later memoirs of Crookes,[1] oluchowski von Smolan[1] and Brush[2] have essenti- contributed.

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[1] *Proc. Roy. Soc.* 1881, xxxi. p. 239.

Winkelmann similarly tested the constancy of the rnal conductivity by determining the logarithmic decre- it of the series of observed readings of his air ther- meter, which decreased with the time in geometrical gression. The following are some of the values found by :—

| | | | |
|---|---|---|---|
| Air . . | Apparatus I . . | $p = 750$ mm. | 0·000509 |
| | | 138 | 501 |
| | | 3 | 480 |
| | Apparatus II . | $p = 750$ | 0·000277 |
| | | 43·3 | 260 |
| | | 13·1 | 260 |
| | | 1 | 259 |
| lydrogen | Apparatus I . . | $p = 750$ | 0·00294 |
| | | 91·9 | 290 |
| | | 4·7 | 258 |
| | | 3 | 245 |
| | | 1·92 | 216 |

ikelmann examined other gases, too, especially ethy- and found a similar confirmation of the law. But the iples we have given will suffice to prove the accuracy of heoretical law and to show us to what low pressures onductivity remains constant.

## Calculation of the Heat-conductivity from the Coefficient of Viscosity

ut the theory requires more than that the value of onductivity should not vary with the density of the it furnishes also the law of the variation of the con- vity with the temperature, and even suggests the ility of calculating the value of the conductivity in absolute units for those gases whose viscosity and specific heat are known. This has been already done by Maxwell and Clausius, the first founders of the theory, long before any measurements of the conductivity of a gas were experimentally made. Clausius concluded from his theory that air conducts heat 1,400 times less well than lead, and Maxwell predicted that the conductivity of air is 3,500 times smaller than that of iron; and both these predictions have been since confirmed in striking fashion by Stefan's experiments.

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[1] ied. *Ann.* 1898, lxiv. p. 101 ; *Phil. Mag.* [5] xlvi. p. 192 ; *Wien. Akad.* r, 36. Jahrg. 1899, p. 1, and *Sitzungsber.* 1899.

[2] il. *Mag.* 1898 [5] xlv. p. 31.

The formula that leads to these conclusions, viz.

$$\mathfrak{k} = 1{\cdot}6027\ \eta c,$$

has yet to be proved. We have to calculate the theoretical value of the conductivity of different gases from the observed values of their coefficient of viscosity $\eta$ and of their specific heat at constant volume $c$, and compare them with the observed values of the conductivity.

The earlier attempts, and even that made in the first edition of this book, to carry out this calculation and comparison led to no perfectly satisfactory results; the calculated and observed numbers exhibited no general agreement together. A satisfactory agreement was obtained only in the case of gases which contain not more than two atoms in the molecule, while with all other gases no approach to agreement was found. This result led to the hypothesis of assuming two different kinds of conduction in gases (§ 105). This faulty attempt to account for the contradiction between theory and experiment was refuted by Wüllner, who saw and proved that the failure to obtain agreement was only due to the faultiness of the values assigned in the formula to magnitudes, the variation of which with temperature was at that time not known with sufficient accuracy, the values employed having been determined at quite different temperatures.

Wüllner,[1] whose memoir has already been several times mentioned in §§ 55–58 of Chapter V., determined anew the ratio of the two specific heats for a series of gases, and investigated the dependence of its value on the temperature.

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[1] *Wied. Ann.* 1878, iv. p. 321.

By combining these measures with the observations of E. Wiedemann on the change which the specific heat $C$ under constant pressure undergoes with change of temperature, he obtained the law of alteration of the specific heat $c$ at constant volume with the temperature, and gave these numbers :—

*Values of c.*

| | 0° C. | 100° C. |
|---|---|---|
| Air | 0·16902 | 0·16930 |
| Carbon monoxide | 17289 | 17395 |
| Carbonic acid | 14886 | 16730 |
| Nitrous oxide | 15130 | 17384 |
| Ethylene | 27007 | 35366 |

Wüllner then combined with these the values of the coefficient of viscosity determined by von Obermayer:—

*Values of η.*

| | 0° C. | 100° C. |
|---|---|---|
| Air | 0·0001678 | 0·0002136 |
| Carbon monoxide | 1625 | 2047 |
| Carbonic acid | 1383 | 1859 |
| Nitrous oxide | 1353 | 1815 |
| Ethylene | 0922 | 1244 |

From this he was then able to calculate the theoretical value of the conductivity $\mathfrak{k}$ for both temperatures and compare them with the values observed by Winkelmann. Wüllner has arranged his results in a table, which I subjoin, with a slight change, by replacing the value $\kappa = 1{\cdot}53$ used by Wüllner, and given in the first edition of this book, by the newly-calculated value $\kappa = 1{\cdot}6027$, whereby the agreement between theory and experiment has for the most part been somewhat improved.

*Values of $\mathfrak{k}$.*

| | 0° C. | | 100° C. | |
|---|---|---|---|---|
| | Calculated | Observed | Calculated | Observed |
| Air | 0·0000455 | 0·0000513 | 0·0000579 | 0·0000653 |
| Carbon monoxide | 450 | 499 | 571 | — |
| Carbonic acid | 330 | 305 | 498 | 466 |
| Nitrous oxide | 328 | 350 | 506 | 506 |
| Ethylene | 399 | 395 | 707 | 636 |

From these numbers, which exhibit a very delightful agreement between theory and experiment, we may also answer the question whether the conductivity $\mathfrak{k}$ really increases as strongly with the temperature as the product of the coefficient of viscosity $\eta$ and the specific heat $c$. For this we need only find the ratio of the values for 100° and 0°, both of the calculated values and of the observed. In this manner Wüllner obtained the annexed table, which shows as good an agreement as can be desired.

*Values of* $\mathfrak{k}_{100}/\mathfrak{k}_0$.

| | Calculated | Observed |
|---|---|---|
| Air . . . . . . . . | 1·275 | 1·277 |
| Carbonic acid . . . . . . | 1·511 | 1·530 |
| Nitrous oxide . . . . . . | 1·541 | 1·447 |
| Ethylene . . . . . . . | 1·767 | 1·611 |

Wüllner has given in his text-book[1] a still more complete table of results. I first extract from this the values of the ratio in which the numbers obtained for 100° by different observers stand to those for 0°. The second column, marked 'calculated,' gives, as in the last table, the ratio of increment of the product $\eta c$ for the change of temperature from 0° to 100°; the last column gives the ratio of increment of the observed values of the conductivity for the same interval of temperature.

*Values of* $\mathfrak{k}_{100}/\mathfrak{k}_0$.

| | Calculated | Observed |
|---|---|---|
| Air . . . . . . . . . | 1·26 | 1·19 – 1·28 |
| Hydrogen . . . . . . . . | 1·24 | 1·175 – 1·275 |
| Nitrogen . . . . . . . . | 1·25 | 1·2 – 1·3 |
| Oxygen . . . . . . . . | 1·26 | 1·2 – 1·3 |
| Carbonic acid . . . . . . | 1·47 – 1·54 | 1·4 – 1·55 |
| Nitrous oxide . . . . . . | 1·54 | 1·33 – 1·45 |
| Ethylene . . . . . . . | 1·75 – 1·78 | 1·6 |

According to this table the differences between the values theoretically determined and experimentally measured are not greater that the errors necessitated by the uncertainty of the observations.

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[1] Wüllner, *Lehrb. d. Experimentalphysik*, ii. 'Wärme' 5. Aufl. 1896, p. 574.

The values of the magnitudes measured at 0° which have been employed for the calculation of these ratios have also been taken from Wüllner's book and are tabulated below. Where Wüllner has given several values I have put down their mean modified by taking $\kappa = 1{\cdot}6027$.

*Values at* 0°.

| | $\eta$ | $c$ | $\kappa\eta c$ | $\mathfrak{k}_W$ | $\mathfrak{k}_G$ |
|---|---|---|---|---|---|
| Air . . . | 0·0001796 | 0·1701 | 0·0000490 | 0·0000561 | 0·0000483 |
| Hydrogen . . | 0885 | 2·4269 | 3442 | 3872 | 3190 |
| Nitrogen . . | 1767 | 0·1738 | 0492 | 0512 | — |
| Oxygen . . | 1959 | 0·1563 | 0491 | 0551 | — |
| Nitric oxide . | 1645 | 0·1665 | 0439 | 0451 | — |
| Carbonmonoxide | 1625 | 0·1732 | 0451 | 0498 | — |
| Carbonic acid . | 1390 | 0·1466 | 0327 | 0335 | 0·0000309 |
| Nitrous oxide . | 1355 | 0·1453 | 0316 | 0353 | — |
| Ethylene . . | 0922 | 0·2782 | 0413 | 0395 | — |

The last two rows contain the values $\mathfrak{k}_W$, $\mathfrak{k}_G$, observed by Winkelmann and Graetz respectively. In the case of three of the gases investigated by both observers, viz. air, hydrogen, and carbonic acid, the theoretically calculated value lies between the two observed values; we may hence assume that the differences still left may be explained merely by the errors of observation, and that they cannot be charged to a defect in the theory.

In Wüllner's table there is only mercury vapour which forms any notable exception. This single exception, however, cannot raise any doubt as to the validity of the law when we consider the uncertainty of the basis of the calculation in this case. The specific heat $c$ of the vapour has not been directly measured, but has been theoretically calculated by the rule given in § 56, from the ratio of the two specific heats and the density deduced from the atomic weight. The coefficient of viscosity $\eta$ has been calculated from the observations of S. Koch,[1] at 273° and 380°, and also for the much lower temperature 203°, for which Schleiermacher[2] has determined the conductivity $\mathfrak{k}$. We may assume that such a process cannot give any certain result, especially if the magnitudes used in the calculation

[1] *Wied. Ann.* 1883, xix. p. 857.

[2] *Ibid.* 1889, xxxvi. p. 346.

are so greatly variable with the temperature as is the viscosity of mercury vapour, according to Koch's formula. It cannot, therefore, be surprising if for mercury vapour the ratio of the observed value of $\mathfrak{k}$ to the calculated value of the product $\eta c$, given by Wüllner, is 3·15, and therefore nearly twice as great as the ratio 1·6027 required by the theory. This great excess of the calculated value of the ratio may be taken as a confirmation of the view put out in § 92, that Koch's numbers are too small because a portion of the mercury vapour may have been condensed into the liquid form in the capillary tube. The behaviour of mercury may also perhaps be explained by the division of the molecules into single atoms (§ 54) not being complete at 203°. But we are in no way compelled to see any obstacle to the theory in this single exception, so long as it is not proved on surer grounds to be an exception.

The excellent agreement of the calculated and observed values shown by all other gases justifies in us, on the contrary, the conviction that the accuracy of the theoretically deduced relation between the conductivity and viscosity of gases is no longer to be doubted, and that we may take it as proved that a gas has the same conductivity for every kind of energy.

From this result of theory we see finally that viscosity, diffusion, and conduction of gases depend in the same way on the free path of the gaseous particles, and that each of these three phenomena may be employed to determine the value of the molecular free path.

# PART III

# ON THE DIRECT PROPERTIES OF MOLECULES

# CHAPTER X

## *ON THE DIRECT PROPERTIES OF MOLECULES*

### 109. Section of the Molecules

As the investigations in Part I. of this book made it possible to calculate in absolute measure the speed of the molecular movements, so the phenomena discussed in Part II. enable us to determine also in absolute measure the length of the paths traversed by the molecules. All the elements therefore which are concerned in the motion of the molecules are fully known.

Still, the conclusions which the theory lets us draw respecting the properties of the molecules are not thereby exhausted; and first of all we may seek to determine the extension of the molecules in space.

When we remember that the length of the paths is determined by the probability of a collision, and that this probability depends on the size of the molecules, it becomes at once clear that the knowledge of their molecular free path enables us to form a judgment as to their extension in space. In 1865, directly after the first experimental investigations of the viscosity of air had led to the knowledge of the free path, Loschmidt[1] made an attempt to determine the sizes of molecules. Later on, in 1867, there appeared two other memoirs with the same aim by my brother Lothar Meyer[2] and Alexander Naumann,[3] then two in 1870 by Lord Kelvin,[1] and in 1873 one by Maxwell.[2]

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[1] *Wien. Sitzungsber.* 1865, lii. Abth. 2, p. 395; *Schlömilch's Zeitschr. f. Math. u. Physik*, 1865, 10th year, p. 511.

[2] *Ann. Chem. Pharm.* 1867, 5. Suppl.-Bd. p. 129.

[3] *Ibid.* 1867, 5. Suppl.-Bd. p. 252.

In the formula found earlier (§ 68) for the free path,

$$L = \lambda^3 / \pi s^2 \sqrt{2},$$

its value is expressed in terms of the size of the elemental cube whose edge has length $\lambda$, and of the diametral section of the sphere of action (§§ 44, 63) whose diameter is $s$. If we use the relation between the size of this cube and the number of molecules contained in unit volume, which is given by

$$N\lambda^3 = 1,$$

the former formula may be written in the shape

$$1 = \sqrt{2}\pi s^2 N L,$$

which shows that, if the free path $L$ is known in absolute measure, the magnitude

$$Q \equiv \tfrac{1}{4}\pi s^2 N = 1/4\sqrt{2}L,$$

or the sum of the diametral sections of the spheres of all the molecules contained in unit volume, can be also expressed in absolute measure.

## 110. Numerical Values

From the values of the molecular free paths as obtained from the observations on viscosity carried out by Graham and by Kundt and Warburg, which are tabulated in § 79, I have calculated the following values of the magnitude $Q$ by the above formula.

*Values of Q.*

| | | | | | |
|---|---|---|---|---|---|
| Air | — | 18400 | Carbonic acid | $CO_2$ | 27000 |
| Hydrogen | $H_2$ | 9900 | Nitrous oxide | $N_2O$ | 27100 |
| Carbon monoxide | $CO$ | 18700 | Sulphurous acid | $SO_2$ | 37900 |
| Nitrogen | $N_2$ | 18600 | Marsh gas | $CH_4$ | 22200 |
| Nitric oxide | $NO$ | 19200 | Ammonia | $NH_3$ | 24900 |
| Oxygen | $O_2$ | 17400 | Ethylene | $C_2H_4$ | 42500 |
| Hydrochloric acid | $HCl$ | 25100 | Methyl ether | $C_2H_6O$ | 43500 |
| Chlorine | $Cl_2$ | 38800 | Methyl chloride | $CH_3Cl$ | 40100 |
| Water vapour | $H_2O$ | 24900 | Cyanogen | $C_2N_2$ | 43900 |
| Sulphuretted hydrogen | $H_2S$ | 29300 | Ethyl chloride | $C_2H_5Cl$ | 49300 |

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[1] *Silliman's Amer. Journ.* 1870, l. pp. 38, 258; *Ann. Chem. Pharm.* 1871, clvii. p. 54; *Nature*, 1883, xxviii. p. 203; *Exner's Repert.* 1885, xxi. pp. 182, 217.

[2] *Phil. Mag.* 1873 [4] xlvi. p. 453; *Ency. Brit.* 9 ed. iii. p. 36; *Scient. Papers*, ii. pp. 361, 445.

The numbers express in square centimetres the sum of the diametral sections for the molecules contained in one cubic centimetre of the gas under the pressure of one atmosphere, or, more correctly, for their molecular spheres of action. What is noticeable in the table at the first glance is the large value of these numbers, which seems to be out of harmony with the assumptions made on the nature of gases. The tabulated number for air, for example, tells us that, if all the molecules contained in a cubic centimetre of air under ordinary pressure could be ranged close together in a plane, they would cover an area of 1·84 square metres with their spheres of action. This large value seems to suggest a rather dense packing of space with the air particles and the assumption that the molecules of bodies cannot be of small size.

It requires, however, but little consideration to see the error in this conclusion. The sum $Q$ of the sections may also attain its value by reason of the largeness of the number $N$ of the molecules, and in this case we should at once be able to conclude that the value of the section of a molecule is really small; for if we consider the number of molecules $N$ to increase by division of the molecules, so that the section of any one molecule becomes correspondingly smaller, yet the sum of the sections will thereby increase. This is easily perceived when we recall the mathematical formulæ for the section and volume of spheres. If, for instance, a sphere is divided into two equal parts, the sum of the sections of the two smaller spheres is greater than the section of the original sphere in the ratio

$$2(\tfrac{1}{2})^{\frac{2}{3}} : 1 = 2^{\frac{1}{3}} : 1 = 1{\cdot}26 : 1.$$

But without mathematical calculation this is easily seen. Suppose we pound a bit of a solid substance to powder, then a larger surface can be strewn with the powder so obtained the finer the powder. We may analogously suppose the molecules of air, which in spite of their light weight can cover so much area as is given above, to form an extremely fine dust, like grains that are very small but of enormous number.

This conception reconciles in the simplest fashion the apparent contradictions between the properties of gases, and explains the striking circumstance that the phenomena—those of viscosity, for instance—remain essentially unaltered even when the gas is very greatly rarefied. For the free path, which a molecule can attain in the fine dust of molecules, remains a small magnitude under all circumstances. It is at once obvious from the numbers given that a cubic centimetre of gas of ordinary density is almost as good as impenetrable by another molecule of gas; but even if this gas has been rarefied to about a three-thousandth part of its normal pressure, and so to a pressure of about $\frac{1}{4}$ mm. of mercury, the number of molecules contained in a cubic centimetre would still yet suffice to thickly cover the six faces of the cube which they fill; this cubical space therefore seems to remain almost as impenetrable as before, and we see that the molecular free path will be still very small even now.

## 111. Section of Compound Molecules

If we compare the tabulated values of the sums of the sections for different gases, we easily perceive that a simple law holds in several cases. The value 25100 for hydrochloric acid is very nearly equal to 24400, which is the arithmetical mean of the values 9900 and 38800 for hydrogen and chlorine respectively. Nitric oxide, however, does not follow this rule, since its value for $Q$, viz. 19200, is greater than the mean (18000) of those for nitrogen and oxygen, viz. 18600 and 17400; but in this case the conformity to the law indicated might be hidden by these three numbers differing from each other by scarcely more than the possible errors of their determination. The same law appears in another similar case; thus the difference of the numbers 27000 and 18700 for $CO_2$ and CO respectively, viz. 8300, is with tolerable exactness the half of the number 17400 found for $O_2$.

These examples seem to indicate that the section of a molecule is equal to the sum of the sections of the atoms which form it; for if this law holds for single molecules, then by Avogadro's law it will hold too for the magnitudes $Q$ which represent the sum of the sections of all the molecules in unit volume. As a test of this supposition I have calculated the most probable values of the sum of the sections of the simple atoms by combining the values found for molecules consisting of only two atoms by the method of least squares, and have obtained the values

$$H = 5082, \quad O = 8877, \quad N = 9513, \quad C = 9796,$$
$$Cl = 19513.$$

By the help of these values, together with those for $H_2S$ and $SO_2$, I have also obtained for the sulphur atom the mean value

$$S = 19617.$$

I have finally from these atomic sections deduced for the compound gases the following molecular sections, which for comparison are tabulated in the column marked 'calculated,' against those given in the former table, and here marked 'observed.'

*Values of Q.*

| | Calculated | Observed |
|---|---|---|
| $H_2$ | 10200 | 9940 |
| $O_2$ | 17800 | 17400 |
| $N_2$ | 19000 | 18600 |
| $Cl_2$ | 39000 | 38800 |
| $HCl$ | 24600 | 25100 |
| $CO$ | 18700 | 18700 |
| $NO$ | 18400 | 19200 |
| $H_2S$ | 29800 | 29300 |
| $CO_2$ | 27500 | 27000 |
| $N_2O$ | 27900 | 27100 |
| $SO_2$ | 37400 | 37900 |
| $NH_3$ | 24800 | 24900 |
| $H_2O$ | 19000 | 24900 |
| $C_2N_2$ | 37600 | 43900 |
| $CH_3Cl$ | 44600 | 40100 |
| $CH_4$ | 30100 | 22200 |
| $C_2H_4$ | 39900 | 42500 |
| $C_2H_6O$ | 59000 | 43500 |
| $C_2H_5Cl$ | 64500 | 49300 |

The two columns exhibit an excellent agreement in the earlier part of the table, but none at all for the last seven compounds. The rule is therefore not of general validity, although it holds in many cases.

## 112. Chemical Structure of Molecules

If the hypothesis were general and exact that the section of the molecule of a chemical compound is equal to the sum of the sections of its atoms, it would allow of but a *single* interpretation, and thereby permit an interesting peep into the circumstances of arrangement of the atoms. We should not be at liberty to make any other assumption than that the atoms which are bound together into one molecule are all in one plane.

We ought, of course, to remark that only the *average* value of the sections can be found from the magnitude of the viscosity of a gas or, more directly, from its mean free path. If now the molecules have a flat shape, then the value of their section, as found by observation, is not identical with the surface-extension of the plane system of molecules. But if we consider in our calculations only the relative and not the absolute measures, we may still be allowed to identify these two sections of the system, the mean and the greatest. For the value of the mean will in this case, in which all others are vanishingly small, be determined almost entirely by the greatest only: hence it seems allowable to extend to the greatest sections the law that holds in many cases for the mean sections.

In all the cases, therefore, in which the calculated values of $Q$ agree with those observed, we shall be able to suppose the grouping of the atoms within the molecule to be such that all the atoms that are bound together in the molecule lie in one plane. We do not need thereby to assume that they are firmly fixed together in this plane, but we may suppose them to be movable in the plane. The system of atoms, then, that form a molecule appears to us as a small planetary system; just as all the planets with their satellites move about the central sun in one and the same plane—at least approximately and with but unimportant exceptions—so the atoms all move in a plane about the centroid of the molecule, and may at the same time rotate about their own axes.

But in one point the similarity between a molecular and a planetary system need not exist. In a planetary system the plane of the motions is unalteringly fixed in space, or else moves so slowly that the change is recognisable only after a long time. But in a molecular system of atoms the plane of motion may be looked upon as variable; indeed it alters its direction at every collision of one molecule with another.

The agreement of the tabulated figures seems to support such a supposition of the condition of the molecules of all gases which are diatomic only. To a pair of atoms of this kind corresponds a double star in the stellar heavens, each part of which describes a plane path about the common centroid.

Further, when three atoms are contained in a molecule we must suppose the molecule to have a plane shape. According to chemists' views the atoms are then so bound together as to be arranged either in a straight line or in a ring. In the last case the plane will be determined by the three points at which the three atoms are. The motion then takes place either by two atoms revolving round the third, or by all three, forming a triangle, revolving about their common centroid. The admissibility of these conceptions arises from the agreement of the calculated with the observed values of $Q$ in all the cases that have been cited, with the single exception of water-vapour; the deviation in this case, however, probably depends only on the observed value not being reducible to the temperature 0° C., to which the other numbers in the table are referred.

When four atoms are joined together to form a molecule it is in general no longer necessary for them to possess the property of being a plane system; the possibility, however, of the system being of such character is shown by the example of ammonia, for which the calculated value of $Q$ agrees very exactly with that observed. We shall consequently be unable to make any other supposition as to the molecular constitution of ammonia than that usual with chemists, viz. that the three atoms of hydrogen are so arranged that their common centroid is always within the atom of nitrogen, and that they circle about this atom in plane orbits.

There is, however, no agreement in general between calculation and experiment for molecules which contain five or more atoms, though in many cases the agreement appears still to hold. This, indeed, is not recognisable from the few cases investigated by Graham, but from the numerous determinations of molecular sections which have been deduced from other observations on viscosity, diffusion, or conduction of heat. I here subjoin some examples which I have taken from a very compendious collection of such numbers, arranged by Landolt and Börnstein.[1]

For marsh gas (or methane), in the case of which the number 22200 for $Q$ deduced from Graham's observations does not agree with that calculated theoretically (30100), we find from Stefan's[2] experiments on diffusion the value 30000, which agrees very exactly with that calculated from the formula $CH_4$. So for chloroform, the same tables assign a value 73700, deduced from one of Puluj's[3] experiments on viscosity, which agrees exactly with that (73400) theoretically calculated from the formula $CHCl_3$. And Graham's number 40100 for methyl chloride $CH_3Cl$ agrees, at least approximately, with the calculated number 44600.

From these examples we may look upon such molecules also as are made up of one tetravalent atom of carbon and four univalent atoms as possessing a plane or, at least, a flat shape. This differs from the usual idea of the grouping in which the four univalent atoms are put at the apices of a regular tetrahedron, at whose centre is placed the carbon atom. If we rely on the assumption that each of the four univalent atoms is bound by the carbon atom in the same way, we can scarcely make any other supposition so long as the atoms are considered at rest. But this conclusion loses its justification if we suppose the gaseous molecule to be in motion and in brisk rotation about its centroid, which lies in the atom of carbon; for the univalent atoms are driven by the centrifugal force into the equatorial plane in which they rotate about the carbon atom. This conception seems to be juster than the other, at least for the state of gas, though the other may, perhaps, better suit the case of the liquid or solid state.

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[1] *Phys.-chem. Tabellen*, 2. Aufl. 1894, tab. 126. But the corrigenda published later must be consulted; from these the numbers quoted are taken.

[2] *Wien. Sitzungsber.* 1872, lxv. Abth. 2, p. 323.

[3] *Ibid.* 1878, lxxviii. Abth. 2. p. 279.

It is not surprising to find that the benzol atom, which we are accustomed to consider ring-shaped, also shows itself to have a plane structure. According to Landolt and Börnstein's tables, the experiments on diffusion by Winkelmann[1] and those on viscosity by Puluj[2] give the values 93000 (W.) and 80350 (P.) for benzol, whereas the value calculated from the formula $C_6H_6$ is 89300. For aceton ($C_3H_6O$) the same tables give 68000 from an experiment by Puluj[3] on viscosity, the calculated number being 68800.

We find[4] also a tolerable agreement for the following group of alcohols:—

*Values of Q.*

| | | Calculated | Observed |
|---|---|---|---|
| Methyl alcohol . . | $CH_4O$ | 39000 | 49000 |
| Ethyl alcohol . . . | $C_2H_6O$ | 59000 | 64700<br>53600 *P* |
| Propyl alcohol . . . | $C_3H_8O$ | 78900 | 87100 |
| Butyl alcohol . . . | $C_4H_{10}O$ | 98900 | 107800 |
| Isobutyl alcohol . . | $C_4H_{10}O$ | 98900 | 105200 |
| Amyl alcohol . . . | $C_5H_{12}O$ | 118800 | 127000 |
| Hexyl alcohol . . . | $C_6H_{14}O$ | 138700 | 159300 |

but a less satisfactory agreement for the ethers:—

| | | | |
|---|---|---|---|
| Methyl ether . . . . | $C_2H_6O$ | 59000 | 43500 *G* |
| Ether . . . . | $C_4H_{10}O$ | 98900 | 89700<br>80380 *P* |

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[1] *Wied. Ann.* 1884, xxiii. p. 203; 1885, xxvi. p. 105.

[2] *Wien. Sitzungsber.* 1878, lxxviii. Abth. 2, p. 279.

[3] *Ibid.* 1878, lxxviii. Abth. 2, p. 279.

[4] All the 'observed' numbers in these four tables are obtained from Winkelmann's experiments on diffusion in the memoir last cited except those marked *P* and *G*, which are deduced respectively from Puluj's experiments on viscosity, or Graham's on transpiration.

while for the following acids we have :—

| | | Calculated | Observed |
|---|---|---|---|
| Formic acid . . . | $CH_2O_2$ | 37700 | 43900 |
| Acetic acid . . . | $C_2H_4O_2$ | 57700 | 59500 |
| Propionic acid . . . | $C_3H_6O_2$ | 77600 | 77900 |
| Butyric acid . . . | $C_4H_8O_2$ | 97600 | 106500 |
| Isovalerianic acid . . | $C_5H_{10}O_2$ | 117600 | 142600 |

Here, too, the deviation is the greater the higher the molecular weight and the greater the number of atoms in the molecule.

Winkelmann's diffusion experiments on a series of esters afford a rich material from which we may draw an answer to the question in hand. They give :—

*Values of Q.*

| | | Calculated | Observed |
|---|---|---|---|
| Methyl formate . . . | $C_2H_4O_2$ | 57700 | 56700 |
| Methyl acetate . . . | $C_3H_6O_2$ | 77600 | 78900 |
| Ethyl formate . . . | $C_3H_6O_2$ | 77600 | 83500 |
| Ethyl acetate . . . | $C_4H_8O_2$ | 97600 | 102000 |
| Methyl propionate . . | $C_4H_8O_2$ | 97600 | 92600 |
| Propyl formate . . . | $C_4H_8O_2$ | 97600 | 98900 |
| Ethyl propionate . . | $C_5H_{10}O_2$ | 117600 | 116300[1] |
| Isobutyl formate . . | $C_5H_{10}O_2$ | 117600 | 86700 |
| Methyl butyrate . . | $C_5H_{10}O_2$ | 117600 | 115500 |
| Methyl isobutyrate . . | $C_5H_{10}O_2$ | 117600 | 111200[2] |
| Propyl acetate . . . | $C_5H_{10}O_2$ | 117600 | 90700 |
| Ethyl butyrate . . . | $C_6H_{12}O_2$ | 137500 | 129300 |
| Ethyl isobutyrate . . | $C_6H_{12}O_2$ | 137500 | 123000 |
| Isobutyl acetate . . | $C_6H_{12}O_2$ | 137500 | 133600 |
| Propyl propionate . . | $C_6H_{12}O_2$ | 137500 | 136300 |
| Ethyl valerianate . . | $C_7H_{14}O_2$ | 157500 | 149000 |
| Isobutyl propionate . . | $C_7H_{14}O_2$ | 157500 | 152400 |
| Propyl butyrate . . | $C_7H_{14}O_2$ | 157500 | 145600 |
| Propyl isobutyrate . . | $C_7H_{14}O_2$ | 157500 | 137700 |
| Isobutyl butyrate . . | $C_8H_{16}O_2$ | 177400 | 165700 |
| Isobutyl isobutyrate . . | $C_8H_{16}O_2$ | 177400 | 165200 |
| Propyl valerianate . . | $C_8H_{16}O_2$ | 177400 | 163700 |
| Amyl propionate . . | $C_8H_{16}O_2$ | 177400 | 177100 |
| Amyl isobutyrate . . | $C_9H_{18}O_2$ | 197400 | 185600 |
| Isobutyl valerianate . . | $C_9H_{18}O_2$ | 197400 | 186500 |

As before, the column of numbers marked 'observed' are deduced from Winkelmann's experiments on diffusion, and are taken from Landolt and Börnstein's tables, while those marked 'calculated' are obtained from the chemical formulæ. There is in general a fairly good agreement between the two columns, which, as in the former cases, is the less the greater the number of atoms combined in the molecule. But differently from what appears in respect to the three other series, the values of the section as calculated from the chemical formulæ are greater than those deduced from the observations, whereas in the other cases it is the observed numbers which mostly are the greater. We shall, therefore, feel inclined to look for the cause of the deviations in the inexactness of the values as deduced from the observations on viscosity or diffusion.

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[1] Another observation gives 87500.

[2] Another observation gives 88400.

In the foregoing I have taken account of all the values given by Landolt and Börnstein which are referred to the temperature 0° C. I have left out only those values that are given for very much higher temperatures; these cannot be brought into agreement with those calculated from the chemical formulæ, and are mostly much the greater. From this we may conclude that the section of compound molecules is very variable with the temperature, and, as we might expect, increases considerably as the temperature rises.

We can, consequently, expect agreement between theory and observation only when all the numbers are reduced to the same temperature. And so good an agreement is exhibited by the great majority of the values at 0° for gases and vapours that we have to conclude in general that *their molecules have a shape that is flat, and not spread out on all sides into space.* This view seems to be the most probable, at least for the gaseous state.

## 113. Molecular Volumes

If the molecules were extended in space on all sides they would behave very nearly as if they were spheres; and no further justification would be needed for looking upon the envelopes, which surround them in such wise that no other molecule can penetrate with its centroid into them, as real spheres and calling them their spheres of action. But, after the foregoing explanations, we must hesitate to believe in the spherical form of the gaseous molecules and, perhaps too, in the spherical form of their spheres of action.

Against this, however, it may be argued that the flat discs which we call molecules are not at rest, but are conceived as being continually in motion; and since, too, they are continuously turning round, they must exert their actions equally in all directions of space, and we should thereby be justified not only in calling the regions within which their action is sensible their spheres of action, but also in looking upon them as veritable spheres.

But we have to consider that the surface conceived to be constructed about a molecule obtains a somewhat different signification when it is assumed to be spherical. The sphere of action has been enlarged to occupy a greater space, which we may call the *molecular volume*; for we may very well so term that volume which a molecule at least requires for itself. If the molecule were at rest, this space would be the sphere of action, or that volume into which the forces exerted by the molecule would not allow another to penetrate; but the molecule is in motion, and requires, therefore, a greater space. This will be smallest when the molecule has no forward velocity and executes only rotatory motions; the rotation of the sphere of action then gives rise to the molecular volume, or the space from which the molecular forces strive to drive intruders now this way and now that. The molecular volume is therefore the smallest space required by the molecule in case it is not quite at rest, or, in other words, robbed of its heat.

What I have here called the molecular volume is not essentially different from that which for many reasons has been denoted by this term in theoretical chemistry. As is well known, chemists call the molecular or specific volume the volume measured in cubic centimetres of a mass which in grams is numerically specified by the same number as the molecular weight. It is therein assumed that the substance is in the liquid state, and consequently in a state that is marked by its very slight compressibility. We may therefore assume that the substances in the liquid state have attained nearly the smallest volumes to which they can be compressed. But the specific volume of a molecule in the liquid state is then exactly the same as that other volume which encloses the sphere of action, and which we have also denominated the molecular volume. The single difference that can still exist is due to the choice of the units in which the numbers are expressed; but this difference also comes to nothing if we content ourselves with relative values and do not strive after a knowledge of the molecular volumes in absolute measure.

When molecular volumes were calculated for the liquid state from the molecular weights and the specific gravities, simple relations were found between the calculated values and the chemical composition of the substances. Kopp,[1] Schröder, and others were led to propose empirical laws, from which the molecular volume of a liquid compound can be calculated by simple addition of the values of the specific volumes of its components.

Loschmidt[2] and Lothar Meyer[3] found similar and just as simple relations when they attempted to estimate the molecular volumes of gases. For this purpose they started from a knowledge of the molecular free paths and of the diametral sections as deduced on the kinetic theory from observations on the diffusion and viscosity of gases. In order to estimate the size of the molecular volume from the section of the sphere of action they neglected the distinction between the sphere of action and the molecular volume, and therefore took the sphere of action as actually spherical.

With this assumption it is very easily possible to compare the volumes of the spheres of action or the molecular volumes

$$V \equiv \tfrac{4}{3}\pi s^3$$

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[1] *Ann. Chem. Pharm.* 1855, xcvi. pp. 1, 153, 303; 1856, c. p. 19.

[2] *Wien. Sitzungsber.* 1865, lii. Abth. 2, p. 395.

[3] *Ann. Chem. Pharm.* 1867, 5. Suppl.-Bd. p. 129.

for different gases; for this purpose the theoretical formula for the coefficient of viscosity (§§ 76, 27),

$$\eta = mG/4\pi s^2 = \sqrt{(3\pi/8)}\, m\Omega/4\pi s^2,$$

or, more strictly by § 78,

$$\eta = 0{\cdot}30967\, m\Omega/\pi s^2\sqrt{2}$$

is of service, in which, as before, $m$ denotes the molecular weight and $\Omega$ the mean molecular speed. For two different gases, which we distinguish by the subscripts 1 and 2, we then obtain the ratio

$$s_1^2 : s_2^2 = m_1\Omega_1/\eta_1 : m_2\Omega_2/\eta_2 = m_1^{\frac{1}{2}}/\eta_1 : m_2^{\frac{1}{2}}/\eta_2,$$

since for equality of temperature we have

$$m_1\Omega_1^2 = m_2\Omega_2^2 \quad \text{or} \quad m_1^{\frac{1}{2}}\Omega_1 = m_2^{\frac{1}{2}}\Omega_2.$$

From this formula we see that the ratio of the sizes of the spheres of action of two gases, viz.

$$V_1/V_2 = (m_1/m_2)^{\frac{3}{4}}(\eta_2/\eta_1)^{\frac{3}{2}},$$

can be determined from the molecular weights and the coefficients of viscosity.

In order to be able to compare the values of the molecular volume calculated by this formula with those given by Kopp, the molecular volume $V_2$ for any normal gas, chosen arbitrarily, with which the others are compared must be put equal to the value found by Kopp. For this purpose Lothar Meyer employed sulphurous acid, because its specific volume seemed to be determined with greater certainty than that of any of the other gases whose viscosity had been accurately measured by Graham. In this way he, and likewise Loschmidt, obtained values for the molecular volume which in many cases agreed really well with those calculated by Kopp from the density of the liquid.

But before I can tabulate the results I must mention a striking circumstance which would be well suited to raise objections against the accuracy of the calculation. Such doubts may be raised even against Kopp's laws, although the molecular volumes of all liquids that had then been investigated with sufficient exactness could be so well calculated by them as to agree excellently with experiment. For there remains the very grave objection that by these rules one and the same volume is not always to be ascribed to one and the same atom. Thus, for instance, the volume of the oxygen atom has to be now 7·8, now 12·2; the nitrogen atom has to have a different volume in ammonia and analogous compounds from what it has in cyanogen compounds, and a third different volume in nitro-compounds.

A further objection is that the molecular volumes calculated for gaseous bodies cannot be represented by the atomic volumes given by Kopp for the liquid state, for this seems to contradict the assumption that the atoms are to be looked upon as invariable. But in order to obtain agreement between calculation and experiment, Lothar Meyer was obliged to assign, both to nitrogen and hydrogen, a different atomic volume in gaseous compounds than in liquid ones.

The variation in the occupation of space by the atoms which we should have to assume in accordance with these investigations can only mean this, that we have not at all to do with the actual dimensions of the atoms and molecules, but with the smallest space which these particles at least require for themselves under the given circumstances. This space may really alter with circumstances. As is almost obvious, it alters with the temperature, because this determines the motion of the atoms. But the shape of the molecule and the grouping of its atoms may also have an influence on the space required by it as a minimum. A flat molecule with its atoms grouped together nearly in a plane will require more room, when turning with its motions that depend on the temperature, than a spherically shaped molecule with its atoms all crowded together. It is thus explicable, from the differences between molecules that have been described, that different extensions in space may be ascribed to the atoms according to their location in the molecule.

The following table contains the results of the different calculations of the molecular volumes :—

*Molecular Volumes.*

| | I | II | III | IV | V |
|---|---|---|---|---|---|
| Air | 15·0 | 15·0 | 15·0 | 25 | 23 |
| Hydrogen | 6·0 | 11·0 | 6·0 | 7 | 7 |
| Carbon monoxide | 15·4 | 23·2 | 18·8 | 25 | 25 |
| Nitrogen | 15·3 | 4·6 | 15·3 | 26 | 24 |
| Nitric oxide | 15·9 | 14·5 | 15·5 | 24 | 23 |
| Oxygen | 13·8 | 15·6 | 15·6 | 22 | 21 |
| Hydrochloric acid | 24·1 | 28·3 | 25·8 | 26·3 | 26·3 |
| Chlorine | 44·1 | 45·6 | 45·6 | 45·6 | 45·6 |
| Water vapour | 28·5 | 18·8 | 13·8 | 18 | 18 |
| Sulphuretted hydrogen | 30·0 | 33·6 | 28·6 | 33 | 33 |
| Carbonic acid | 26·7 | 31·0 | 26·6 | 36 | 35 |
| Nitrous oxide | 26·7 | 16·8 | 27·5 | 37 | 35 |
| Sulphurous acid | 43·9 | 42·6 | 42·6 | 48 | 48 |
| Ammonia | 23·6 | 18·8 | 16·7 | 23·5 | 22·5 |
| Marsh gas | 19·4 | 33·0 | 23·0 | 35 | 28 |
| Cyanogen | 55·1 | 56·0 | 56·0 | 54 | 56 |
| Methyl chloride | 48·2 | 50·3 | 42·8 | 47·3 | 47·3 |
| Ethylene | 33·6 | 44·0 | 34·0 | 42 | 42 |
| Ethyl chloride | 66·0 | 72·3 | 59·8 | 68·3 | 68·3 |
| Methyl ether | 53·8 | 62·8 | 47·8 | 60 | 60 |

Column I. gives the values of the volume of the sphere of action, taken as spherical, on an arbitrary scale ; these were calculated by Lothar Meyer from Graham's experiments on transpiration. We must further remark that the mean molecular weights of the components of air have been employed for the calculation of the number given for air, and also that the number for water-vapour, which I have added, has been deduced from Kundt and Warburg's experiments on viscosity.

Column II. contains the values, calculated by Kopp's rules, of the molecular volume in the liquid state. For the volumes of an atom are taken

$$\begin{array}{lll} S = 22{\cdot}6 & C = 11{\cdot}0 & N = \phantom{2}2{\cdot}3 \\ Cl = 22{\cdot}8 & H = \phantom{1}5{\cdot}5 & CN = 28{\cdot}0, \end{array}$$

and it is assumed that $O = 7{\cdot}8$ in free oxygen, water vapour, and methyl ether, and $O = 12{\cdot}2$ in carbon monoxide, nitric oxide, and nitrous oxide ; further, that in carbonic acid and sulphurous acid the two atoms together have the value $7{\cdot}8 + 12{\cdot}2 = 20{\cdot}0$.

Column III. contains the values which result from

Lothar Meyer's assumed occupation of space by the atoms. The volumes N = 7·7 and H = 3·0 are assumed, and also O = 12·2 in nitrous oxide and for one of the atoms in sulphurous acid, but in all other cases O = 7·8.

Columns IV. and V. contain the values as calculated in accordance with Loschmidt's assumptions. In them are put

$$S = 26, \quad C = 14, \quad Cl = 22{\cdot}8, \quad H = 3{\cdot}5,$$

and in Column IV.

$$O = 11, \quad N = 13,$$

but in Column V.

$$O = 11, \quad O_2 = 21, \quad N = 12, \quad CN = 28.$$

The agreement of the last four columns with the first is not complete, and indeed cannot be if the preceding considerations are justified; for here the sphere of action and the molecular volume are treated as if the same thing, whereas in reality the former is much the smaller. If the theory were worked out with absolute accuracy, we should have to deal with circumstances which depend not only on the volume, but also on the section and shape of the molecular system; hence no perfect regularity of agreement can show itself if the matter is treated one-sidedly as if the volume alone determined the phenomena.

But so many cases exhibit a surprisingly good agreement that all idea of the agreement being accidental must be put aside. One will agree with Lothar Meyer in deducing from his figures that *the atomic volumes of many elements in their liquid combinations are proportional to the spaces occupied by their atoms in the gaseous state.*

## 114. Influence of the Molecular Heat-motion in Liquids on the Apparent Size of the Molecular Volume

One feels oneself tempted to go a step further in this conclusion, and to assume that the volumes in the liquid and gaseous states are not only proportional to, but identical with, each other. Lothar Meyer did not consider this conclusion justified, but he is of opinion that the molecular and atomic volumes are greater in the liquid state than in the gaseous. The weightiest reason that he adduces for this view rests on a conception, like that of our gaseous theory, of the state of motion which the molecules of a liquid take in consequence of their heat.

We have to consider the atoms in lively motion not only in the gaseous state, but also in the liquid and solid states. The solid state seems to be characterised by the centroids of the molecules being at rest while the atoms move. Dulong and Petit's law at least points to this, in so far as it establishes a relation for the atomic heat of different bodies into which the molecular heat does not enter at all. We shall probably have to conceive of the liquid state as something between the other two; so that we have to ascribe to the particles of a liquid both molecular and atomic motions. Of whatever kind these motions may be,[1] they in any case require space for their performance. In a liquid, therefore, a molecule will, under all circumstances, require a larger space than if it were at rest.

The space demanded by a molecule will presumably increase, not only with the kinetic energy but also with the speed itself, in such a way that, of two different kinds of molecules whose energies are equal, the lighter needs a larger space for its correspondingly quicker motion than the heavier and therefore more slowly moving molecule. The same holds good for the atoms. By this consideration Lothar Meyer explains the behaviour, for instance, of hydrogen, for which a much smaller atomic volume results from consideration of its viscosity than Kopp had calculated for it from its liquid compounds; and this was his reason for assigning to hydrogen in gaseous molecules a smaller volume than in molecules of a liquid.

Similar considerations may enter into the case of other atoms, even if, perhaps, they are less striking. We may therefore assume it as possible, for the molecules built up of atoms, that their molecular volume in the liquid state is larger than in the gaseous.

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[1] On this subject further explanations will be found in Clausius' memoir, *Pogg. Ann.* 1857, c. p. 360; *Abhandl.* 2. Abth. 1867, p. 236.

In spite of all this, we have no reason to believe that the molecules themselves are larger in a liquid than in the vapour of the same substance. For, to explain the difference of the two states of aggregation, the assumption that the motion of the molecules in the two cases is different seems sufficient. If the molecular motion in liquids were known to us just as much as the motion in gases; we should be in as good a position for liquids as for gases to determine in absolute measure the sum of the sections, or any other corresponding property, of the whole assemblage of molecules contained in unit volume, and we could thus by experiment decide the question with certainty whether the difference of the states of aggregation consists only in the motion or also in other properties of the molecules. But so long as we are without a kinetic theory of the liquid state, we cannot in the determination of the extension in space of the molecules bring into the calculation the influence of their motion, as in the case of gases, and we therefore obtain values which are too high.

## 115. Possibility of Determining the Size of Gaseous Molecules

We have succeeded, however, in obtaining limiting values, at least, of the sizes of molecules in absolute measure by comparison of the two fluid states of aggregation. Such a calculation was first attempted and made by Loschmidt,[1] and then later by Lord Kelvin[2] (then Sir William Thomson) and by Maxwell[3] in the memoirs already cited.

These calculations assume the sphere of action to be spherical, and they are based on the relation between the mean free path $L$ and the radius $s$ of the sphere of action, which was discovered by Clausius, and is with Maxwell's theory represented by the formula

$$1 = \sqrt{2}\pi s^2 NL$$

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[1] *Wien. Sitzungsber.* 1865, lii. Abth. 2, p. 395.

[2] *Nature,* 1870, i. p. 551; *Silliman's Amer. Journ.* l. pp. 38, 258.

[3] *Phil. Mag.* 1873 [4] xlvi. p. 453; *Scient. Papers,* ii. 1890, p. 361.

that we have already (§ 109) employed. This may be written in the form

$$s = 6\sqrt{2} \,.\, \tfrac{1}{6}\pi s^3 N \,.\, L,$$

wherein the value of $s$, which may also be called the diameter of the molecule, is expressed by magnitudes of simple signification. Since $\frac{1}{6}\pi s^3$ is (§ 109) the volume of the molecular sphere, the product $\frac{1}{6}\pi s^3 N$ denotes the space actually occupied by the molecules contained in unit volume.

Let $\mathfrak{v}$ denote the ratio of this volume to the unit volume in which the molecules are contained, or

$$\mathfrak{v} \equiv \tfrac{1}{6}\pi s^3 N : 1 = \tfrac{1}{6}\pi s^3 N\,;$$

we shall with Loschmidt call it the *coefficient of condensation,* since underlying it is the meaning that it represents the extreme limit of possible condensation. We thus obtain for the molecular radius the formula

$$s = 6\sqrt{2}\;\mathfrak{v}L,$$

which allows the possibility of a calculation in absolute measure, if we may assume that when a gas is transformed into a liquid it has actually reached its maximum condensation; for in this case the value of the coefficient of condensation would be given simply by the ratio of the densities of the substance in the gaseous and liquid states.

This assumption is certainly not free from doubt, since, in the first place, the assumption of the spherical shape is not justified, and in the second, as we have remarked in the foregoing paragraph, the space required by a molecule in the liquid state is possibly, or probably, not equal to the extension of the molecule in space when actually in the gaseous condition. The values of the coefficient of condensation $\mathfrak{v}$ so obtained will thus presumably be too large, and this must also be true of the values of the molecular diameter $s$ which are calculated on this assumption. Such a calculation is not, however, valueless, because it at least shows us that the gaseous molecules must be less than a certain magnitude which is expressed in absolute measure.

## 116. Values of the Molecular Diameter

The calculation of the molecular diameter $s$ may be actually carried out for a large number of gases and vapours, since now not only their mean free paths are known from measurements of viscosity and diffusion, but also their densities in the liquid state.

I first of all tabulate the necessary data as to density in the liquid state of the series of gases whose free paths are sufficiently well determined from viscosity experiments; and when several determinations are to hand for the same material I shall always choose the greatest, as this is to be preferred for our purpose.

For the density of liquid sulphurous acid Is. Pierre[1] found the value 1·49 at − 20°; for liquid ammonia A. Lange[2] obtained the value 0·6954 at − 50°; for liquid carbonic acid Cailletet and Mathias[3] found 1·057 at − 34°, and the same observers[4] determined the value 1·003 for nitrous oxide at − 20·6°. The density of liquid ethyl chloride is given as 0·9216 at 0° by Is. Pierre,[5] 0·9176 at 8° by Linnemann,[6] 0·9253 at 0° by Darling[7]; of these values I use the greatest 0·925. For methyl chloride Vincent and Delachanal[8] found the density 0·9831 at − 20°.

Faraday[9] has found 0·866 for the density of cyanogen in the liquid state, and 0·9 for the approximate density of condensed sulphuretted hydrogen.[10] Ansdell[11] found for hydrochloric acid 0·908 at 0°.

The density of liquid chlorine at − 80° is given as 1·6602 by Knietsch,[12] and Cailletet and Mathias[13] found that of liquid ethylene at − 21° to be 0·414. Wroblewski[14] measured the density of liquefied oxygen at − 200°, and found the value 1·24; Olszewski[1] has likewise determined the density of nitrogen at − 181° as from 0·859 to 0·905, and that of marsh gas at − 164° as 0·4148. And, finally, Dewar[2] obtained for the density of liquid hydrogen at its boiling-point, − 238°, the sixfold smaller value 0·07.

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[1] *Ann. Chim. Phys.* 1847 [3] xxi. p. 336.

[2] *Zeitschr. f. Kälte-Ind.* 1898, v. p. 39; *Wied. Beibl.* xxii. p. 265.

[3] *Journ. de Phys.* 1886 [2] v. p. 555.

[4] *Ibid.* 1886 [2] v. p. 555.

[5] *Ann. Chim.* 1845 [3] xv. p. 362.

[6] *Ann. Chem.* 1871, clx. p. 214.

[7] *Ibid.* 1869, cl. p. 221.

[8] *Comptes Rendus*, 1878, lxxxvii. p. 987; *Ann. Chim.* 1879 [5] xvi. p. 427.

[9] *Phil. Trans.* 1845, p. 169; *Pogg. Ann.* 1848, Erg. Bd. ii. p. 215.

[10] *Phil. Trans.* 1823, p. 193.

[11] *Chem. News*, 1880, xli. p. 75; *Wied. Beibl.* 1880, iv. p. 310.

[12] *Ann. Chem.* 1890, cclix. p. 100.

[13] *Journ. de Phys.* 1886 [2] v. p. 555.

[14] *Comptes Rendus*, 1886, cii. p. 1010.

With these values of the density $\delta$ for the substances in the liquid state I have combined the numbers giving the density $\Delta$ in the gaseous state, and from their ratio I have calculated the coefficient of condensation

$$\mathfrak{v} = \Delta / \delta .$$

I have, however, not employed the observed values of the density $\Delta$ of the gases, but their values as theoretically calculated from their molecular weight $M$ by means of the formula[3]

$$\Delta = M / (28{\cdot}88 \times 773{\cdot}3) .$$

I consider this procedure the more correct as it gives the smallest values for $\Delta$, and therefore also the smallest possible values for the coefficient of condensation $\mathfrak{v}$.

In order to now find from these values of $\mathfrak{v}$ the values of the diameter $\mathfrak{s}$ I have employed the numbers for the free path $L$ which I have deduced from Graham's observations and have tabulated in § 79. The following table contains the results of this calculation :—

| | $\delta$ | $\mathfrak{v}$ | $10^7\mathfrak{s}$ cm. |
|---|---|---|---|
| Hydrogen | 0·07 | 0·00203 | 3·06 |
| Marsh gas | 0·4148 | 266 | 1·81 |
| Ammonia | 0·6954 | 173 | 1·04 |
| Ethylene | 0·414 | 477 | 1·70 |
| Nitrogen | 0·905 | 219 | 1·76 |
| Oxygen | 1·24 | 182 | 1·57 |
| Sulphuretted hydrogen | 0·9 | 267 | 1·36 |
| Hydrochloric acid | 0·908 | 282 | 1·70 |
| Carbonic acid | 1·057 | 293 | 1·62 |
| Nitrous oxide | 1·003 | 311 | 1·71 |
| Methyl chloride | 0·9831 | 368 | 1·38 |
| Cyanogen | 0·866 | 424 | 1·44 |
| Sulphurous acid | 1·49 | 303 | 1·21 |
| Ethyl chloride | 0·925 | 488 | 1·49 |
| Chlorine | 1·6602 | 301 | 1·17 |

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[1] *Wied. Beibl.* 1886, x. p. 686.

[2] *Proc. Chem. Soc.* 1898, p. 146; *Wied. Beibl.* 1898, xxii. p. 515.

[3] Lothar Meyer, *Mod. Theor. d. Chemie*, 6. Aufl. Breslau 1896, p. 36.

I have deduced similar values from the observations on viscosity of Kundt and Warburg,[1] and also of Puluj,[2] and of these I quote the following :—

| | | $M$ | $\delta$ | $\mathfrak{v}$ | $10^6 L$ cm. | $10^7 \varsigma$ cm. |
|---|---|---|---|---|---|---|
| Water . . . | $H_2O$ | 17·88 | 1·0000 | 0·00282 | 9·7 | 1·70 |
| Aceton . . . | $C_3H_6O$ | 57·61 | 0·8125 | 503 | 2·60 | 1·11 |
| Carbon disulphide . | $CS_2$ | 75·55 | 1·29215 | 415 | 2·90 | 1·02 |
| Benzol . . . | $C_6H_6$ | 77·46 | 0·899 | 612 | 2·20 | 1·13 |
| Chloroform . . | $CHCl_3$ | 118·48 | 1·5264 | 551 | 2·40 | 1·12 |

Winkelmann's[3] observations on diffusion afford a rich material for the calculation of further values. For these I have, as before, made use of the numbers given in Landolt and Börnstein's tables.

| | | $M$ | $\delta$ | $\mathfrak{v}$ | $10^6 L$ cm. | $10^7 \varsigma$ cm. |
|---|---|---|---|---|---|---|
| Ether . . . | $C_4H_{10}O$ | 73·52 | 0·736 | 0·00709 | 1·97 | 1·19 |
| Carbon disulphide . | $CS_2$ | 75·55 | 1·29215 | 415 | 2·55 | 0·90 |
| Benzol . . . | $C_6H_6$ | 77·46 | 0·899 | 612 | 1·90 | 0·99 |
| *Acids* | | | | | | |
| Formic acid . . | $CH_2O_2$ | 45·67 | 1·245 | 0·00260 | 4·03 | 0·89 |
| Acetic acid . . | $C_2H_4O_2$ | 59·58 | 1·08005 | 392 | 2·97 | 0·99 |
| Propionic acid . | $C_3H_6O_2$ | 73·49 | 0·9961 | 524 | 2·27 | 1·01 |
| Butyric acid . . | $C_4H_8O_2$ | 87·40 | 0·9886 | 628 | 1·66 | 0·88 |
| Isovalerianic acid . | $C_5H_{10}O_2$ | 101·31 | 0·9467 | 760 | 1·24 | 0·80 |
| *Alcohols* | | | | | | |
| Methyl alcohol . | $CH_4O$ | 31·79 | 0·796 | 0·00284 | 3·61 | 0·87 |
| Ethyl alcohol . . | $C_2H_6O$ | 45·70 | 0·794 | 409 | 2·73 | 0·95 |
| Propyl alcohol . | $C_3H_8O$ | 59·61 | 0·8205 | 516 | 2·03 | 0·89 |
| Butyl alcohol . . | $C_4H_{10}O$ | 73·52 | 0·8239 | 633 | 1·64 | 0·88 |
| Isobutyl alcohol . | $C_4H_{10}O$ | 73·52 | 0·8168 | 639 | 1·68 | 0·91 |
| Amyl alcohol . . | $C_5H_{12}O$ | 87·43 | 0·8296 | 748 | 1·39 | 0·88 |
| Hexyl alcohol . . | $C_6H_{14}O$ | 101·34 | 0·8333 | 863 | 1·11 | 0·81 |
| *Esters* | | | | | | |
| Methyl formate . | $C_2H_4O_2$ | 59·58 | 0·9928 | 0·00426 | 3·12 | 1·13 |
| Methyl acetate . | $C_3H_6O_2$ | 73·49 | 0·9562 | 546 | 2·24 | 1·04 |
| Ethyl formate . . | $C_3H_6O_2$ | 73·49 | 0·9447 | 552 | 2·12 | 0·99 |
| Methyl propionate . | $C_4H_8O_2$ | 87·40 | 0·9573 | 648 | 1·91 | 1·05 |
| Ethyl acetate . . | $C_4H_8O_2$ | 87·40 | 0·8981 | 691 | 1·73 | 1·01 |
| Methyl isobutyrate . | $C_5H_{10}O_2$ | 101·31 | 0·9056 | 794 | 1·59 | 1·07 |
| Methyl butyrate . | $C_5H_{10}O_2$ | 101·31 | 0·9475 | 759 | 1·53 | 0·99 |
| Ethyl propionate . | $C_5H_{10}O_2$ | 101·31 | 0·9139 | 787 | 1·52 | 1·01 |
| Propyl acetate . . | $C_5H_{10}O_2$ | 101·31 | 0·910 | 790 | 1·95 | 1·31 |

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[1] *Pogg. Ann.* 1875, clv. p. 540. Compare § 79.

[2] *Wien. Sitzungsber.* 1878, lxxviii. Abth. 2, p. 279.

[3] *Wied. Ann.* 1884, xxiii. p. 203 ; 1885, xxvi. p. 105.

| | | $M$ | $\delta$ | $\mathfrak{v}$ | $10^6 L$ cm. | $10^7 \varsigma$ cm. |
|---|---|---|---|---|---|---|
| Isobutyl formate . | $C_5H_{10}O_2$ | 101·31 | 0·8845 | 813 | 2·04 | 1·41 |
| Ethyl butyrate . | $C_6H_{12}O_2$ | 115·22 | 0·8978 | 911 | 1·37 | 1·06 |
| Ethyl isobutyrate . | $C_6H_{12}O_2$ | 115·22 | 0·890 | 919 | 1·44 | 1·12 |
| Propyl propionate . | $C_6H_{12}O_2$ | 115·22 | 0·9022 | 907 | 1·30 | 1·00 |
| Ethyl valerianate . | $C_7H_{14}O_2$ | 129·13 | 0·894 | 1025 | 1·19 | 1·04 |
| Propyl butyrate . | $C_7H_{14}O_2$ | 129·13 | 0·8789 | 1043 | 1·22 | 1·08 |
| Isobutyl butyrate . | $C_8H_{16}O_2$ | 143·04 | 0·8798 | 1154 | 1·07 | 1·05 |

The values we have found of the magnitude $s$, which may, perhaps, be looked upon as the diameter of a gaseous molecule, are almost all approximately equal, and most of them do not differ by so much as one-millionth of a millimetre. Hence it would seem that all gaseous molecules and their spheres of action have nearly equal sizes.

But if we recall the manifold uncertainties in the assumptions upon which our conclusions rest, we must hesitate to consider this result of the calculations as a certainly proved truth. And some of the numbers that differ from 1 must certainly give rise to doubt.

For hydrogen—that is, for the gas with just the least density and the least molecular weight—the calculation has given the greatest value for the diameter. It is possible that the reason for this striking circumstance lies only in this, that at $-238°$ the liquefied hydrogen has not yet attained its highest density. But there still remains the suspicious circumstance that the greatest values of the diameter are found just for the simplest chemical compounds, and especially for those of them whose molecular weight is small.

We easily see that such relations between the weight and diameter of molecules cannot in general correspond to actuality if we try to employ the numbers we have here obtained to calculate that magnitude which Loschmidt terms the volume of the molecular path. He understands by this, as we have already mentioned in § 69, the volume of the space which a molecule occupies while it traverses its straight free path, and thus the volume of the cylinder, whose section is that of the molecule, viz. $\frac{1}{4}\pi s^2$, and whose height is the free path $L$. According to the assumptions of our theory, the product of these two magnitudes ought to have a constant value. But we do not at all find this constancy when we proceed to calculate the path-volume for a series of gases from the foregoing numbers.

It therefore follows that we cannot hold ourselves justified in taking the calculated values of $s$ as representing the actual diameters of the gaseous molecules. The reason that we may not do so is obvious. There can be no doubt that the molecules are not spheres in shape; for, as we concluded in § 112 from a large number of facts, they are more probably, without exception, flattish discs of very small thickness. We therefore cannot arrive at true values of their diameter and volume by looking on them as spheres. At most we may expect (§ 113) to obtain from this calculation an estimate of the volume of a larger sphere which the flat disc describes when it rotates, and the mean diameter of a molecule must be less than the diameter of this sphere. We may not, therefore, take the values calculated for $s$ as giving the true size of the molecules, but may see in them only a superior limit which the size of the molecules does not attain.

From these considerations we can conclude only that the gaseous molecules are smaller than a sphere whose diameter is one-millionth of a millimetre. But we may add as very probable that the size of the gaseous molecules will in no way appear to be vanishingly small when compared with that small sphere. This is justified on many other grounds, which we have still to mention.

## 117. Calculation of the Size of Molecules from the Deviations from Boyle's Law

The above calculated numbers obtain a remarkably good confirmation from the values which we obtain for the same magnitude by a different mode of calculation first given by van der Waals.[1] In the theory explained in Chapter IV. of this book, by which van der Waals sought to explain the deviations of actual gases from the Boyle-Gay Lussac law, the grounds of these deviations were found partly in the cohesion of the gases and partly in the space occupied by their molecules. On the basis of this theory the values of two constants $a$ and $b$, the latter of which represents a measure of the size of the molecules, could be calculated from Regnault's observations on the compressibility of gases and on their expansibility under the action of heat.

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[1] 'Over de continuïteit van den gas- en vloeistof-toestand,' Leiden 1873, transl. by Phys. Soc. London, 1890, Chap. VI. p. 384. Abstracted in *Beibl.* to *Pogg. Ann.* 1877, i. p. 10.

This magnitude $b$ is directly connected with the coefficient of condensation $\mathfrak{v}$ described in the last paragraph, and to recognise this more clearly we will seek with van der Waals to push Clausius' theory of the molecular free path a step further. The correction, which is calculated in fuller detail in § 34* of the Mathematical Appendices, results from regard being paid to the fact that a particle cannot pass over paths between other particles which are equal to the distances apart of these other particles, or, more strictly, of their centroids; for the paths cannot be greater than the length left free between the spheres of action of the particles. For this reason the estimated molecular free path,

$$L = \lambda^3 / \pi s^2 \sqrt{2},$$

has to be diminished by an amount which depends on the radius $s$ of the sphere of action. This correction attains its greatest value when the collision is direct and central, in which case the paths of both colliding molecules are together shortened by the radius $s$. On the average its value is smaller, and equal to

$$(\sqrt{2}/3)\, s,$$

so that the free path would, strictly speaking, be represented by the formula

$$L = (\lambda^3 - \tfrac{2}{3}\pi s^3) / \pi s^2 \sqrt{2}.$$

From this we see that the so-called elemental cube $\lambda^3$, in which a *single* molecule is contained, is diminished in the corrected formula by

$$\tfrac{2}{3}\pi s^3 \equiv 4 . \tfrac{1}{6}\pi s^3,$$

that is, by four times the volume of the molecular sphere.

From this remark we at once obtain the meaning of the constant $b$ which comes into van der Waals's theory, since on this theory a similar correction was introduced by putting the smaller volume $v - b$ for the larger volume $v \equiv N\lambda^3$ of the whole mass consisting of $N$ molecules. The number to be subtracted has thus the meaning

$$b = 4.\tfrac{1}{6}\pi s^3 N,$$

that is, it is equal to four times the volume actually occupied by the whole of the molecules that are contained in unit volume.

Putting in this equation the value of the free path given by the former formula

$$1 = \sqrt{2}\,\pi s^2 NL,$$

which may without hesitation be here employed without correction, we obtain

$$bL = (\sqrt{2}/3)s,$$

so that we can calculate the molecular diameter $s$ from the known values of $b$ and $L$. In this calculation we have still one precaution to take; for $b$ and $L$ are both dependent on the pressure, $b$ being proportional to the number $N$ and therefore to the pressure, and $L$ being inversely proportional to these magnitudes. The values given in §§ 79 and 116 for the free path have reference to the pressure of one atmosphere, while the values of $b$ calculated by van der Waals and others from his theory presuppose, at least for the greatest part, the pressure of 1 metre of mercury; to compensate for this difference we must multiply the formula for the calculation of the radius of the sphere of action by the ratio of the pressures, and thus put

$$s = (3/\sqrt{2})\,pbL,$$

where $b$ is referred to the pressure of 1 m. of mercury, and $p$ denotes the pressure in metres of mercury for which the value of $L$, which is employed, holds good.

From the observations made by Regnault and Cailletet on the deviations of gases from Boyle's law, van der Waals[1] has calculated the following values:—

| | |
|---|---|
| Air . . . . . . | $b = 0{\cdot}0026$ |
| Carbonic acid . . . . | 30 |
| Hydrogen . . . . . | 069 |

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[1] *Continuïteit, &c.* Chap. VIII. b. §§ 41, 42, pp. 67–9. Phys. Soc. Transl. pp. 400–2. F. Roth, *Wied. Ann.* 1880, xi. p. 25.

On combining with these the values of the free paths given in §§ 78 and 79, as obtained from Graham's experiments on transpiration, we obtain for the molecular diameters the values:

| | |
|---|---|
| Air . . . | $s = 0{\cdot}80 \times 10^{-7}$ cm. |
| Carbonic acid . | $0{\cdot}63$ ,, |
| Hydrogen . . | $0{\cdot}40$ ,, |

These numbers are markedly smaller than those given before, but they are of the same order of magnitude, and therefore we may see in them a confirmation of the correctness of the theoretical views from which we have started.

We should obtain a better agreement if we replaced the numerical factor of the formula, $3/\sqrt{2} \equiv 2{\cdot}12$, by a greater value. Our determination of this factor really rests on a not entirely safe footing, and it has not always, therefore, come out the same.[1] We might object that the correction, which the value of the free path needs on account of the space occupied by the spheres of action, must not be applied quite in the same way as that which we have to make to Boyle's law for the same reason. The two corrections, therefore, $b$ and $4 \cdot \frac{1}{6}\pi s^3 N$, need not be equal to each other, but may still differ by a numerical factor; and this factor is obtained by Clausius[2] and G. Jäger[3] from the consideration that molecules which are near each other cannot be struck by another colliding particle at every point of their surface if they really occupy space; there is therefore a diminution of their surface to be taken into account in the calculation, and this consideration leads to the formula

$$b = \tfrac{5}{2} \cdot \tfrac{1}{6}\pi s^3 N,$$

---

[1] In the first edition of this book another smaller value, 1·5, was taken; this results from assuming as strictly valid the calculation first developed in § 34* of the Mathematical Appendices. There are grounds of probability in its favour which depend on the phenomena described in § 118 (Heilborn, *Exner's Repert.* 1891, xxvii. p. 369; Sydney Young, 1898, *Chem. News*, lxxviii. p. 200), but the larger value seems to me to be theoretically better established.

[2] *Mech. Wärmetheorie*, 1889–91, iii. pp. 57, 213; *Wied. Ann.* 1880, x. p. 102.

[3] *Wien. Sitzungsber.* 1896, cv. Abth. 2, p. 97.

from which we get for the determination of $s$ the formula

$$s = (24/5\sqrt{2})\, bL.$$

The factor, according to these theories, becomes $24/5\sqrt{2} \equiv 3{\cdot}39$, and attains therefore a value by which a satisfactory agreement is established.

## 118. Calculation of the Size of the Molecules from the Dielectric Capacity

Stefan,[1] in his memoir on the theory of the diffusion of gases, drew attention to a simple relation in which the values of the mean free paths of the gaseous molecules stand to the refractivities of the gases. He remarked that the refractive index $n$ of a gas is the smaller the greater the free path $L$ of its molecules, the simple law, indeed, that the product

$$(n-1)L$$

has a nearly constant value, holding for many gases, especially for those whose properties have been investigated with the greatest exactness.

Now Maxwell's electromagnetic theory of light requires the refractive index of a substance to be equal to the square root of its dielectric capacity; and this law has been shown by Boltzmann's[2] experiments on seven gases to be very exactly correct. Therefore also the dielectric capacity of a gas must stand in as simple a relation to the mean free path of its molecules as its refractive power.

The surprising fact that a simple connection exists between two such different magnitudes as the dielectric capacity and the molecular free path finds its explanation in an assumption regarding the molecular qualities of dielectric bodies made by Faraday and by Mossotti. The molecules of such substances are assumed to be good conductors of electricity, while the interspaces between them are taken to be insulating. According to this assumption the dielectric polarisation must depend on the size and distance apart of the molecules, and therefore on the same elements which regulate the molecular free path. This explanation makes the connection of the two magnitudes to appear no longer surprising.

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[1] *Wien. Sitzungsber.* 1872, lxv. Abth. 2, p. 341. Compare also Rubenson, *Oefv. Kgl. Vetensk.-Akad. Forhandl. Stockholm*, 1884, xli. No. 10, p. 3.

[2] *Pogg. Ann.* 1875, clv. p. 421.

Clausius[1] has developed the theory of these relations after the method of Maxwell and Helmholtz. His theory, with the assumption that the molecules are spherical in shape and are perfect conductors of electricity, gives the dielectric capacity $K$ in the form

$$K = (1+2g)/(1-g),$$

where $g$ denotes the fraction of the volume containing the gas which its molecules actually occupy. By transformation then we obtain the value of $g$ expressed in terms of the dielectric capacity $K$, viz.

$$g = (K-1)/(K+2).$$

We see at once that this magnitude $g$ is closely allied in its meaning to the coefficient of condensation $\mathfrak{v}$ introduced by Loschmidt; for both ratios represent exactly the same thing if the molecules come into actual contact in their utmost state of compression. But it is possible, and even probable, that the spherical surfaces on which the electric charges of the molecules reside, do not come into actual contact with each other, even when the molecules are on the point of entering within the range of their spheres of action. The fraction denoted by $g$ may therefore be less than that denoted by $\mathfrak{v}$, and can at most be equal to it.

If, therefore, we replace $\mathfrak{v}$ in Loschmidt's formula

$$s = 6\sqrt{2}\,\mathfrak{v}L$$

by $g$, we shall probably obtain a smaller value for the molecular diameter $s$ than is given by either Loschmidt's or van der Waals's formula. Dorn[2] is the first who has carried out this calculation of $s$ by the formula

$$s = 6\sqrt{2}\,gL = 6\sqrt{2}\,L(K-1)/(K+2),$$

and he combined the values of the dielectric capacity $K$

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[1] *Mechanische Wärmetheorie*, 1879, 2. Aufl. ii. p. 94.

[2] *Wied. Ann.* 1881, xiii. p. 378.

etermined by Boltzmann, as well as one observation by yrton and Perry, with the values of the molecular free aths $L$ calculated from Graham's experiments on transiration. The numbers found by him are really much maller than those obtained by the other modes of calculaon, as we see from the following comparison of his numbers ith those calculated by the methods of Loschmidt (§ 116) nd van der Waals (§ 117).

*Values of* $10^7 s$ *in cm.*

| | Dorn | Loschmidt | v. d. Waals |
|---|---|---|---|
| Air . . . . . . | 0·16 | — | 0·80 |
| arbonic acid . . . | 0·18 | 1·62 | 0·63 |
| Hydrogen . . . . . | 0·14 | 3·06 | 0·40 |
| arbon monoxide . . | 0·19 | — | — |
| Nitrous oxide . . . | 0·18 | 1·71 | — |
| thylene . . . . . | 0·21 | 1·70 | — |
| Marsh gas . . . | 0·23 | 1·81 | — |
| ulphurous acid . . | 0·69 | 1·21 | — |

We might therefore consider it possible that Dorn's umbers represent too small values of the molecular ameters, and that they even form an *inferior* limit, as oschmidt's give a *superior* limit, for the magnitude $s$, hose true value lies somewhere between the two. I will t contest the admissibility of this idea, but I must consider very uncertain, as so many kinds of unproved and even probable assumptions underlie all these calculations. The pothesis that the molecules are shaped like spheres, which curs in the discussion of their dielectric behaviour, seems to to be especially doubtful; for the dielectric polarisation l, if the molecules are of a flat shape (§ 112), be entirely ferent from what it will be if they are spheres.

Franz Exner[1] and Ph. Guye[2] have devoted atten n to these relations, in addition to Dorn. The former ves extensive tables of values, among which are some at have been calculated from the indices of refraction served by Dulong. For the fraction $g$ can be calculated not only from the dielectric constant $K$ by means of the relation

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[1] *Wien. Sitzungsber.* 1885, xci. Abth. 2, p. 850; *Exner's Repert.* 1885, p. 446.

[2] *Arch. d. Sc. Phys. et Nat.* 1890 [3] xxiii. p. 197.

$$g = (K - 1)/(K + 2),$$

but also from the index of refraction $n$ by means of the analogous formula

$$g = (n^2 - 1)/(n^2 + 2),$$

which on Maxwell's theory is identical with it. To avoid repetitions I will cite these figures only from Exner's memoir.

*Values of* $10^7 s$ *in cm.*

| | | | |
|---|---|---|---|
| Ammonia | 0·16 | Sulphuretted hydrogen | 0·22 |
| Water vapour | 0·09 | Hydrochloric acid | 0·18 |
| Nitrogen | 0·17 | Cyanogen | 0·19 |
| Nitric oxide | 0·16 | Sulphurous acid | 0·17 |
| Oxygen | 0·16 | Chlorine | 0·19 |

These numbers, too, like those calculated by Dorn from the dielectric capacity, are considerably less than those which were deduced from the coefficients of condensation, and from the deviations from Boyle's law. They agree in magnitude with Dorn's values with striking accuracy, since, almost without exception, they are equal to 0·2 millionth of a millimetre. Sulphurous acid is the only exception to this rule in Dorn's table, and in his opinion this is due to inaccuracy in the value of the dielectric capacity used in the calculation; and since Exner's value is much smaller, we may fall in with Dorn's conjecture.

We must therefore consider it established that, if electrical or optical measurements are employed in the calculation of the diameter of the molecular sphere of a gaseous molecule, the value

$$s = 0{\cdot}2 \text{ millionth of a millimetre}$$

is found on the average. On the contrary we find

$$s = 1 \text{ millionth of a millimetre}$$

at least, if we rely upon observations within the domain of mechanics. We should not pretend to see any agreement in these numbers, which vary in the ratio 1 to 5, if we had to do with magnitudes which are capable of direct measurement. But since these magnitudes are much smaller than the smallest that is microscopically visible, and since a knowledge of them is attainable only in roundabout ways by the use of many kinds of measures and uncertain conclusions, we must rejoice and, at least provisionally, be content that we have found values which differ only so little from each other that they, in all cases, are of the same order of magnitude.

We shall be able to form a judgment with greater certainty as to the trustworthiness of these figures when we shall have compared them with the values deduced from different speculations (§ 122). But we may now attempt to decide the question, which method of determining the absolute magnitude of the molecules deserves preference over the other. The answer can scarcely be doubtful if we remember that the determination by means of the mechanical measurements cannot give too small, but only too large values of the molecular diameter. The smaller of the values found is therefore to be looked upon as the more credible, and I therefore use the value

$$s = 0{\cdot}2 \times 10^{-7} \text{ cm.}$$

in some further conclusions as to the state of gaseous molecules.

But there is still a further reason which we may give for preferring the values calculated from the dielectric capacities and the refractive indices. The equality of the path-volume (§ 69), which the former values failed to give (§ 116), comes into view when the latter are employed in the calculation, as is proved with sufficient accuracy by the following values of the product $s\sqrt{L}$ calculated by Dorn:—

| | |
|---|---|
| Air . . . . . . | 1·55 |
| Carbonic acid . . . . | 1·42 |
| Hydrogen . . . . | 1·84 |
| Carbon monoxide . . . | 1·86 |
| Nitrous oxide . . . . | 1·50 |
| Ethylene . . . . | 1·56 |
| Marsh gas . . . . | 2·12 |

These numbers have for unit of length the millionth part of a millimetre.

## 119. Section and Volume of Molecules

Although we may not pretend to see an exact evaluation of the size of the molecular diameter in the value 0·2, which we have assumed as a mean, yet it seems justifiable to suppose that this number may serve as an approximately correct estimate. It is therefore not lost trouble, and it is more than a play with figures, if we calculate the sectional area and the volume of a molecule from this estimate of its diameter. We shall be conscious that the calculation can give us only approximate values, since we must once more introduce the assumption of a spherical figure, which is not strictly correct.

If, then, we put $s = 2 \times 10^{-8}$ cm. as the average diameter of a gaseous molecule, its sectional area will be $\frac{1}{4}\pi s^2 = 3 \times 10^{-16}$ sq. cm., and its volume $\frac{1}{6}\pi s^3 = 4 \times 10^{-24}$ ccm. Referred to the millionth part of a millimetre as unit of length, these numbers are 0·2, 0·03, 0·004 respectively, the units of area and volume then being the face and volume of a cube of which the edge is a millionth of a millimetre.

## 120. Number and Distance apart of Molecules

Now that we have attained to a knowledge of the size of the molecules, there opens out the possibility of taking a further step towards the knowledge and measurement of an invisible world by determining first the value of $N$, or the number of molecules contained in unit volume. This is at once obtained if we compare the value of the sectional area just computed with the sum of the sections $Q$, discussed in § 109, which we likewise know in absolute measure, having calculated it numerically in § 110. By this magnitude $Q$ we understand the area covered when we range close together on a plane all the molecules contained in one cubic centimetre of a gas under atmospheric pressure. Since we now know, at least approximately, the size of the covering spheres, in addition to the area covered, it is easy to calculate the number of spheres which we wish to find.

In this calculation I shall content myself again with an approximate estimate. If the area of a molecule is about $3 \times 10^{-16}$ sq. cm., while the molecules contained in 1 cubic centimetre of air can cover an area of 18400 sq. cm., their number is

$$N = 18400/(3 \times 10^{-16}) = 61 \times 10^{18},$$

or in 1 cubic centimetre of air under atmospheric pressure there are about 60 trillion molecules. This number holds not only for air, but also, by Avogadro's law, for all gases under the pressure of one atmosphere.

From this number we at once obtain also the value of the mean distance apart $\lambda$ of two neighbouring molecules by means of the formula

$$N\lambda^3 = 1,$$

whence

$$\lambda = 2{\cdot}6 \times 10^{-7} \text{ cm.} = 2{\cdot}6 \text{ millionths of a millimetre};$$

and this number, too, is the same for all gases under atmospheric pressure.

The values we have found confirm in a remarkable way a conjecture which Clausius made so early as 1858 in his celebrated memoir on the molecular free path. In this paper, which has formed the starting-point for the investigations now occupying our attention, Clausius[1] estimates the fraction of the space, enclosing a gas which is actually filled by the spheres of action when the pressure is that of one atmosphere, as about one-thousandth, this estimate being given for the explanation of his ideas by a numerical example. Clausius, therefore, puts $\lambda^3 = 1000 . \frac{4}{3}\pi s^3$, whence it follows that $\lambda = 16 s$; and he further finds $L = 61 \lambda$ from his formula for the free path.[2]

If we find the corresponding relations with the values that we have now obtained from observations, we have in round numbers for air $L = 0{\cdot}00001$ cm., and therefore

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[1] *Pogg. Ann.* 1858, cv. p. 250; *Abhandl.* 2. Abth. 1867, p. 273.

[2] Compare § 65.

$L = 40\lambda$ about. We further find, since $s = 2 \times 10^{-8}$ cm., the relation $\lambda = 13\,s$, and, finally, we obtain for the volume actually filled by the molecules contained in 1 cubic centimetre under atmospheric pressure,

$$N.\tfrac{1}{6}\pi s^3 = 2{\cdot}5 \times 10^{-4} \text{ ccm.} = \tfrac{1}{4} \text{ cubic millimetre};$$

the molecules themselves therefore fill only about a 4,000th part of the whole space containing them. The spheres of action of Clausius, of which $s$ is the radius and not the diameter, occupy a volume eight times larger than the molecules, and therefore about a 500th part of the whole volume.

The agreement with the numbers assumed by Clausius is so close that the good fortune with which he chose his example would appear wonderful if we had not rather to see in it a testimony to his sure and clear vision into things.

If we calculate the values of these magnitudes for very small pressures such as occur in Geissler's tubes, *i.e.* for a pressure of about 1 mm. of mercury, the number of molecules in 1 cubic centimetre will be 760 times less, or $N = 80000$ billions about; it thus remains still very large, and we see again that a space containing gas which is so extremely rarefied is still very far indeed from being completely empty.[1] In this case the mean distance apart of two neighbouring molecules is $\lambda = 23$ millionths of a millimetre about.

We can also raise the question as to how these relations alter when the gas is very highly compressed. At a pressure of 1,000 atmospheres the distance between neighbouring molecules would become $\lambda = 0{\cdot}26$ millionths of a millimetre, so that the molecular spheres must then be nearly in contact with each other. But, as we have several times remarked, we must not leave out of account the fact that our numbers represent only limiting values; $s$ may very well be less than we have calculated it, and in this case $N$ would have to be taken still larger, while $\lambda$ on the contrary would diminish, though not so much as $s$, since the value of the free path $L$ is not altered by such change of $s$.

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[1] Compare §§ 84 and 110.

## 121. Absolute and Specific Weight of Molecules

Remembering this possibility, it will not appear an unallowable boldness to attempt also, as van der Waals and Maxwell have done, to calculate the mass of a molecule in absolute measure, or at least to determine a limiting value of it.

From the number of molecules in 1 cubic centimetre of a gas which we now know, we obtain very simply the mass of a single molecule by dividing by this number the mass of the gas contained in 1 cubic centimetre, which is the same number as that representing the density of the gas relatively to that of water. Since air under atmospheric pressure is 770 times lighter than water, it follows that there will be about 770 × 60 or 46,000 trillion molecules of air in 1 gram, or 46 trillions in 1 milligram; or the mass of a molecule of air is about $2 \times 10^{-23}$ gram.

From this we can also calculate the density of a molecule of air, since we know the size of the molecules; for we have the mass of a 46-trillionth of a milligram contained in a volume of 0·004 trillionth of a cubic millimetre, so that the specific gravity of the actual substance of an air molecule referred to water is 5, which is considerably greater than the specific gravity of air in the liquid state.

Hydrogen is about fourteen times lighter than air, and there are therefore about 640 trillions of hydrogen molecules in 1 milligram; the unit of the usual atomic weights is thus equal to about a 1,300-trillionth of a milligram, or, as we may more shortly express it, a quadrillion of hydrogen atoms weigh about $\frac{3}{4}$ gram.

## 122. Comparison with other Limiting Values

Having arrived at the end of these investigations, we will not omit to compare the last remarkable conclusions that have been deduced from the kinetic theory of gases with the results of other methods by which attempts have been made to compass the weighing and measuring of molecules and atoms.

The most direct judgment as to the smallness of the atoms is afforded by investigations on the limits to which the divisibility of matter can be pushed. For this purpose strongly-coloured substances have been employed, and these have been diluted by solution until their colour has disappeared. By experiments of this kind Musschenbroek, Achard, and other older physicists,[1] as also A. W. Hofmann[2] in later years, have shown that coloured substances can be plainly recognised when diluted to a 100-millionth, or even less, of their strength, from which we may conclude that the smallest quantity that can be weighed can be divided into several hundred million parts. Annaheim[3] has calculated in this way that an atom of hydrogen must weigh less than 0·05 millionth of a milligram [which is $6 \times 10^{15}$ times our calculated mass]. It is obvious that this method is not suitable for obtaining the *outside* limit of divisibility, but the experiments are interesting as showing that the numbers calculated in the foregoing paragraphs are really much smaller than the limit attained.

The same may be said of an experiment by Kirchhoff and Bunsen,[4] by which it was proved that a 3-millionth part of a milligram of sodium chloride is sufficient to colour the flame of a Bunsen burner distinctly yellow.

In a similar way attempt has been made to push the ductility[5] of a substance to the utmost, in order thereby to obtain a limit for the size of the smallest particles. Faraday[6] has obtained gold leaves whose thickness he estimates as 100 times less than the length of a wave of light; since these leaves must contain at least one layer of atoms, it follows that the thickness of an atom of gold is equal to or less than 5 millionths of a millimetre. This limit corresponds sufficiently accurately to the size of the gaseous molecules which we have obtained from the kinetic theory, viz. 0·2 millionth of a millimetre for the diameter of a molecule.

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[1] The older literature has been put together by Muncke in *Gehler's Wörterbuch*, 1838, ix. p. 709, article 'Theilbarkeit,' and by G. Karsten in the *Encyklopädie der Physik*, edited by him, 1869, i. pp. 820, 877.

[2] *Ber. d. deutsch. chem. Ges.* 1870, p. 660.

[3] *Ibid.* 1876, ix. p. 1151.

[4] *Pogg. Ann.* 1860, cx. p. 168.

[5] Compare the article 'Dehnbarkeit' in *Gehler's Wörterbuch*, 1826, ii. p. 504.

[6] *Pogg. Ann.* 1857, ci. p. 318.

The experiments by which it has been attempted to determine the size of the spheres of action of the molecular forces in liquids, or the distance to which capillary forces sensibly extend, also afford help towards the answering of our question. For this purpose Plateau[1] measured the smallest thickness at which films of a soap solution containing glycerine could still hold together; he took a half of this thickness as the range of the molecular forces, and thus obtained the value 0·00005 mm. This value of the range of the molecular forces was also found by Quincke[2] by measuring the thickness of thin layers on a wall which exerted capillary force on a liquid through the thin layer. Sohncke[3] proceeded by Plateau's method, and measured the smallest thickness of a layer of oil which spread itself over the surface of a liquid; he, like Plateau and Quincke, also found 0·00005 mm. for the semi-thickness. But shortly after Röntgen[4] showed that it is possible to obtain much thinner layers of oil; he observed layers of only 0·56 millionth of a millimetre which held together, so that the range of the capillary forces in Plateau's sense would be only 0·3 millionth of a millimetre, and would consequently agree almost exactly with the diameter of the molecular sphere of a gaseous particle. Drude[5] found that, when a film made of Plateau's soap solution has become so thin as to show no colour, but blackness only, it is 17 millionths of a millimetre thick at this point, so that the range of the capillary forces would be half of this, or 8½ millionths of a millimetre.[6] Reinold and Rücker[7] had, by measurements of its electrical resistance, found the thickness of such a film to be 12 millionths of a millimetre. Bunsen,[1] and also Warburg and Ihmory,[2] found magnitudes of the same order by weighing the films of water formed on glass. But long before all these experiments were made Thos. Young, as Lord Rayleigh[3] has pointed out, instituted measurements for the determination of the range of the capillary forces, for which he found a 250-millionth of an inch, *i.e.* 0·1 millionth of a millimetre, but by a calculation that is really uncertain.

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[1] *Mém. de Brux.* 1861, xxxiii. p. 44; 1847, xvi. p. 35.

[2] *Pogg. Ann.* 1869, cxxxvii. p. 402.

[3] *Münch. Sitzungsber.* 1890, xx. p. 93; *Wied. Ann.* 1890, xl. p. 345.

[4] *Wied. Ann.* 1890, xli. p. 321.

[5] *Ibid.* 1891, xliii. p. 158.

[6] Johonnott estimates $6 \times 10^{-6}$ mm. (*Phil. Mag.* 1899 [5] xlvii. p. 501).

[7] *Proc. Roy. Soc.* 1877, xxvi. p. 334; *Wied. Ann.* 1891, xliv. p. 778.

Lord Kelvin[4] found just as small a value as these for the volume of the molecules of a liquid by discussing in another way the phenomenon examined by Plateau, viz. the formation of thin films of liquid. He investigated the work required to extend a liquid film, and also the corresponding amount of heat, and found from these considerations that inconceivable conclusions would follow if we were to assume that several layers of the ultimate atoms of water were to lie over each other in a water film the thickness of which is twenty times less than a millionth of a millimetre. Boltzmann[5] calculated the work which is necessary for a displacement of the particles that are held together by capillary forces, and compared it with the tenacity of the substance in the solid state; this consideration led to the result that the range of molecular forces in metals lies between 1 and 7 millionths of a millimetre. By similar considerations De Heen[6] concluded, from a comparison between the tension of a capillary surface and the pressure of the vapour above it, that the radius of the sphere of action for water is about 3 millionths of a millimetre. On the contrary, G. Jäger[7] obtained the values 0·5 for water and alcohol, 0·4 for methyl alcohol, 0·7 for aceton and carbon disulphide, 0·8 for ether and chloroform, all expressed in millionths of a millimetre. He starts with the assumption that we may consider the molecules as small drops which result from larger ones that are broken up by collisions with each other and with the sides of the containing vessel. Such a division of a drop into two smaller ones is possible only when the kinetic energy of the collision is greater than the work which must be spent in overcoming the forces of cohesion and producing the increase of the capillary surface that results from the division. Since both the kinetic energy of the molecules and the intensity of the capillary pressure are known, the limit at which divisibility ceases can be determined. Houllevigue[1] and H. A. Wilson[2] tried to find the same limit by determining the conditions under which the latent heat of vaporisation and the capillary pressure of a drop of water equilibrate each other; and the results of both give 0·13 millionth of a millimetre as the smallest diameter which a drop of water can have.

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[1] *Wied. Ann.* 1885, xxiv. p. 321.

[2] *Ibid.* 1886, xxvii. p. 481.

[3] *Phil. Mag.* 1890 [5] xxx. p. 474.

[4] *Proc. Roy. Soc.* 1858, ix. p. 255.

[5] *Wien. Sitzungsber.* 1877, lxxv. Abth. 2, p. 801.

[6] *Bull. Ac. Belg.* 1892 [3] xxiii. p. 235; *Wied. Beibl.* 1892, xvi. p. 724.

[7] *Wien. Sitzungsber.* 1891, c. Abth. 2, p. 1233; *Wied. Beibl.* 1892, xvi. p. 345; Winkelmann's *Handbuch d. Physik*, 1896, ii. Abth. 2, p. 602.

Phenomena can be adduced from other branches of physics, such as optics, for example, which may serve to give a determination of the size of the smallest particles. Our first idea would be to get an estimate of it from the size of the smallest objects that are visible microscopically; but the limit of visibility is, unfortunately, reached far too soon in consequence of the diffraction of light in the microscope, so that only a 4,000th part of a millimetre is recognisable.[3] The dispersion of light can, on the contrary, be utilised for an estimation in this respect, as it is caused by the action of the material particles on light; and Lord Kelvin[4] has so employed it. It is sufficient to mention here that the simple laws of dispersion in transparent media cannot be correct if only a few particles are to be found in the length of a wave of light. If there are many, the distance separating two neighbouring particles must be much smaller than the length of a wave of light, and if the number were 1,000 we should have 0·0005/1000 mm. for the distance between adjacent particles; and this agrees fully with the value determined by the theory of gases. A far better estimation, which rests on similar assumptions, is the calculation from the refractive index of a gas, which has already been mentioned in § 118.

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[1] *Journ. de Phys.* 1896 [3] v. p. 159.

[2] *Chem. News*, 1896, lxxiii. p. 63.

[3] Helmholtz, *Pogg. Ann.* 1884, Jubelband, p. 557.

[4] *Nature*, 1870, i. p. 551.

In addition to the method, described also in § 118, of calculating the size of molecules from the values of the dielectric capacity, there are also other ways of determining it by electrical measurements. For this we can make use of considerations which compare the energy of the electrical forces brought into play with other kinds of energy, just, indeed, as those we have mentioned in respect of the capillary forces. By comparing his measurements of the force of attraction between a pair of plates of zinc and copper, which are electrified by contact with each other, with the equivalent amount of heat, Lord Kelvin[1] finds that it cannot be possible to make plates of these metals, whose thickness is 30 times less than a millionth of a millimetre. The atoms of zinc and copper, therefore, like the molecules of air, have a size that is measurable in millionths of millimetres. L. Lorenz[2] also makes use of the electrical potential energy of a zinc-copper element and the value of the energy necessary for the electrolysis of water, and from these data he draws the conclusion that the mean distance apart of two molecules of water in the liquid state must be at least 10 times less than a millionth of a millimetre. Oberbeck,[3] who investigated experimentally the electromotive forces of thin layers, found that the molecular forces of platinum are perceptible through layers of other metals of from 1 to 2 millionths of a millimetre in thickness.

If these different methods that have been used to obtain a limit of the divisibility of matter do not all lead to the same value for the size of the particles, they yet agree, without exception, in giving the thickness of an atom or molecule of the substances investigated as not much less than a millionth of a millimetre. We may, therefore, consider ourselves justified in looking upon this measure as a tolerably accurate limit of the size of the smallest particles.[1]

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[1] *Proc. Roy. Soc.* 1860; *Nature*, 1870, i. p 551, ii. p. 56.

[2] *Pogg. Ann.* 1870, cxl. p. 644.

[3] *Wied. Ann.* 1887, xxxi. p. 337.

## 123. Molecular Forces

The information given by the kinetic theory as to the forces that act between atoms and molecules seems very meagre in comparison with the widely extending knowledge of their state which this theory affords.

We know as a fact, directly proved by experiment, that the forces exerted by gaseous molecules on each other when separated by their average distances are of very small intensity. But this tells us nothing as to the same forces which come into operation between two molecules when they approach very near to each other. Our theory assumes that forces come into play at a collision which drive the molecules away from each other; but, however much we have discoursed of impacts and impulses in this book, we have learnt nothing more as to the nature of these forces; we have remained in ignorance whether these forces are instantaneous stresses, which come into play at the moment of contact, or if they are of the kind generally assumed in theories of capillarity, which act at only very small distances and rapidly fall off as the distance increases, while, on the other hand, preventing a diminution of the distance beyond a certain limit.

If the theory of gases does not decide this question, it is no ground for reproach of the theory; but, on the contrary, it is the source of a superiority which this theory has over others. For the reason that it does not decide the question which of the two hypotheses on the nature of molecular forces, which seem possible and admissible, is the true one, is that it is itself independent of the choice of either of these hypotheses. The kinetic theory of gases is based on firmer ground than that it should stand or fall with one of these hypotheses.

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[1] [An admirable *résumé* of the experimental investigations on molecular magnitudes is contained in Rücker's lecture 'On the Range of Molecular Forces.' *Journ. Chem. Soc.* 1888, liii. p. 222.—TR.]

Even though a decision respecting these hypotheses is therefore not necessary for our theory, the question still arises, whether absolutely no hypothesis at all as to the process of an encounter has been introduced into our demonstration or general assumptions have tacitly been made. The answer lies in the remarks which I have made in § 25 with respect to the basis of Maxwell's law, as to the distribution of the different values of the speed among the individual molecules.

Some general theorems of analytical mechanics have in fact been introduced into our reasoning as the conditioning assumptions upon which that important law rests; first and foremost the *proposition of the conservation of energy*, then some less important theorems which are generally looked upon as conditions of that proposition, viz. the theorem of the *equality of action and reaction*, and, lastly, the theorem of the *conservation of the motion of the centre of gravity* of two molecules both before and after an encounter. In addition to these, the hypothesis has also been made that the *duration of an encounter is very small* in comparison with the interval between two encounters. Other assumptions were not necessary.

The assumptions enumerated are all satisfied, both if the molecules are perfectly elastic and if they act on each other with forces which fall off very rapidly as the distance increases and which are therefore only sensible at exceedingly small distances. They can also be fulfilled with other laws of impact, as, for instance, when two absolutely hard bodies collide, the hardness of which, together with the impossibility of compressing them, causes a repulsive force to come suddenly into play at the moment of the collision.

This follows from Poinsot's[1] investigations on impact, so far as his results relate to perfectly elastic and absolutely hard bodies. The correctness of this view is seen more clearly from a memoir by Gustav Lübeck,[1] who investigates the laws of the collision of massive particles without introducing any further suppositions than the above-named theorems. It follows that these assumptions are sufficient to determine the velocities with which the colliding particles separate from each other after an encounter when the velocities which the particles possessed before the encounter are known. We easily see, for instance, without calculation for direct impact, that from the two propositions of the conservation of kinetic energy and of the conservation of the motion of the centre of gravity we obtain two equations, which must be sufficient to fully determine the two unknown values of the velocities after the impact. The same thing holds in the more general case of oblique impact, in which only the number of unknown magnitudes is greater since several components come into account.

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[1] Liouville's *Journ. de Math.* [2] 1857, ii. p. 281; 1859, iv. p. 421; Schlömilch's *Zeitschr. f. Math. u. Physik*, 1858, 3. Jahrg. pp. 143, 274.

We may from this conclude that the validity of the laws which determine the change of the motions on the occurrence of an elastic impact is not confined to the case of elastic bodies, but presupposes only that the above-named theorems of mechanics hold good. *We may therefore assume that the laws of elastic impact are valid for the encounters of molecules also without thereby ascribing elasticity to the molecules themselves.*

If according to this the answer to the question, what forces are developed at an encounter of two gaseous molecules, does not touch the foundation of the kinetic theory, that question still remains so important and interesting that we cannot pass it over in silence.

In memoirs upon this theory, and especially in the older ones, we often meet with the assumption that two molecules behave during an encounter like two elastic bodies, or even like two elastic spheres. This hypothesis has much that is tempting about it from the ease with which it can be handled; but the difficulty would only be transferred, and not overcome, if we proposed to explain the elasticity of gases by the elasticity of the molecules.

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[1] Schlömilch's *Zeitschr. f. Math. u. Physik*, 1877, 22. Jahrg. p. 126.

In order, therefore, to explain the behaviour of the gaseous particles, we must have recourse to the assumption of forces which the particles exert on each other, at least when near enough; and there arises only the question whether these forces are attractive or repulsive; for the latter may also come into play when the distance becomes small enough, though the gaseous molecules certainly attract each other at their mean distances of separation.

On this account Maxwell, too, for a long time defended the assumption of repulsive forces between gaseous particles. These repulsive forces were supposed to decrease more rapidly than the attractive forces as the distance increased, and, indeed, inversely in proportion to the fifth power of the distance, while the attractive forces were to be taken as following Newton's law of being inversely proportional to the square of the distance. Maxwell[1] arrived at this hypothesis, which allows of a very easy and elegant treatment, because the law of dependence of the viscosity of a gas on the temperature, which is deduced from this hypothesis, is that which he obtained by experiment. But since this law, viz. that the coefficient of viscosity of a gas is proportional to the absolute temperature, is contradicted by later observations, the hypothesis must be given up.

Other physicists have professed the view that attractive forces are to be assumed as acting between gaseous molecules. That such forces must be assumed unconditionally has been proved by Clausius by means of his proposition of the Virial, from which it follows that a stationary state of motion can be permanently maintained only if forces maintain the equilibrium dynamically, and that therefore a stable state is quite impossible without attractive forces.[2] Further, Boltzmann[3] has shown that it is also sufficient to assume *only* attractive forces, and no repulsive forces, between gaseous molecules. By assuming that strongly attractive forces act only at quite small distances, he obtains the very same laws for an encounter which Maxwell obtained with his repulsive forces. This result is in excellent agreement with Lübeck's proposition, of which we have made mention. We may therefore consider all the forces as attractive which gaseous molecules exert upon each other, whether at large or small distances apart. This corresponds to the experimental results of Joule and Lord Kelvin as to the heat-effects of flowing gases, and also no less to the ideas employed by Sutherland to explain the large variation of the coefficient of viscosity with the temperature.

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[1] *Phil. Trans.* 1867, clvii. p. 49; *Phil. Mag.* 1868 [4] xxxv. p. 129; *Scient. Papers*, ii. p. 26.

[2] *Bull. Ac. Belg.* 1886 [3] xi. p. 193; *Kinetische Theor. d. Gase*, 1889–91, p. 264.

[3] *Wien. Sitzungsber.* 1884, lxxxix. Abth. 2, p. 714; *Wied. Ann.* 1885, xxiv. p. 37.

The law of variation of the strength of these attractive forces with the distance between the particles cannot yet be decided from our present knowledge. It is, however, quite possible to calculate, or at least to estimate, the amount of the energy that comes into play during the action of these unknown forces. This is just as possible as it was possible to estimate the energy of the heat contained in a body without its being necessary to know the law of the molecular movement in which heat consists.

Boltzmann[1] has made a first essay in this direction, and has thereby proved that we have to do with forces of extraordinarily great intensity. In this calculation Boltzmann introduces manifold hypothetical suppositions which are approximately admissible for every case; we may especially mention that, just as we did in former paragraphs, he looks upon the molecules themselves as the same in the liquid and gaseous states, and upon their motions only as different.

With Boltzmann we will first of all calculate the amount of energy needed for two molecules of water, whose mean distance apart is $\rho$, to approach each other by the length $x\rho$, so that their distance apart is reduced to $(1 - x)\rho$. For this we make use of a result of Grassi's experiments on the compressibility of liquids, viz. that water is compressed by 0·000048 of its volume by the pressure of one atmosphere, so that by the addition of an atmosphere to the pressure the distance apart $\rho$ of two molecules is diminished by $0{\cdot}000016\rho$. An atmosphere is the pressure of 10334 kilograms per square metre, and it therefore exerts on the area $\rho^2$ corresponding to a single molecule the force $10334 g\rho^2$ absolute units, wherein the kilogram is taken as unit of mass and the metre as unit of length, $g$ being the acceleration of gravity. Since this force diminishes $\rho$ by $0{\cdot}000016\rho$, the force required to diminish $\rho$ by $x\rho$ is

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[1] *Wien. Sitzungsber.* 1872, lxvi. Abth. 2, p. 213.

$$10334 g\rho^2 x / 0{\cdot}000016,$$

if we may make the assumption (which is doubtless approximately correct) that the force is directly proportional to the amount of approach. The work done by this force while the molecules are approaching each other is found by multiplying the force by half the diminution of distance, and it is therefore

$$10334 g\rho^3 x^2 / 0{\cdot}000032.$$

Boltzmann compares this expenditure of work with the energy of the molecular motion in water-vapour, in order to determine the shortening of distance, measured by $x$, which occurs at a collision of two molecules. Let $m$ be the mass of a molecule, and therefore, with a kilogram and a metre as units, $m \equiv 1000\rho^3$, since 1 cubic metre of water weighs 1000 kilograms; further, with our former notation, wherein $G$ represents the mean value of the molecular speed as calculated from the energy, the sum of the kinetic energies of the two colliding molecules is

$$2.\tfrac{1}{2}mG^2 = mG^2,$$

where by § 28 the value of $G$ for water-vapour at the temperature 0° is to be taken as 614 metres per second.

If we equate the value of the energy so determined to the above value found for the expended work, and also put $g = 9{\cdot}81$, we have

$$1000 \times 614^2 \rho^3 = 10334 \times 9{\cdot}81 \rho^3 x^2 / 0{\cdot}000032,$$

whence we obtain

$$x = 1/2{\cdot}9 = \tfrac{1}{3}$$

in round numbers, so that

$$1 - x = \tfrac{2}{3}.$$

According to this calculation the centres of two molecules of water-vapour at 0°, if they undergo direct collision when moving with their mean kinetic energy, approach to a distance of $\frac{2}{3}\rho$, which is only two-thirds of their separation when they are in the liquid state at maximum density at 4°. In order to compress water so strongly, a pressure of 20,000 atmospheres must be employed.

Though several points in this calculation may have only a very doubtful justification, yet from the result we learn that the molecular forces which are developed on the encounter of two molecules possess a very considerable intensity.

From the value of the molecular energy we can at once form an estimate of the energy of the motion of the atoms within the molecule; for the ratio in which these two energies stand to each other is (§ 53) determined by the ratio of the two specific heats. The forces, therefore, to which the atoms are subject must also be in general very great.

The only exception is that of the case when the molecule is monatomic. In this case we might assume that there is not interior motion at all in the molecule, since it is simple and consists of but one atom. But this assumption cannot be right, for monatomic gases and vapours—mercury vapour, for instance—can radiate light the spectrum of which consists of a series of bright lines, and therefore internal motions must be present in a gaseous molecule that contains but one atom just as in a polyatomic molecule.

Eilhard Wiedemann[1] has cleared up this apparent contradiction by measuring the energy necessary to make a vapour luminous. He compared the light radiated by sodium vapour with that coming from a platinum wire made to glow by the passage of an electric current; from the resistance of the wire and the strength of the current he could determine the luminous energy in heat units, and compare it with the total heat-energy contained in the vapour. He found that the energy needed for the illumination is vanishingly small in comparison with the total energy. An atom, therefore, must be a structure in which pendulous movements can be produced by very small forces.

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[1] *Wied. Ann.* 1889, xxxvii. pp. 241, 248.

## 124. Vortex Atoms, Pulsating and Electrical Atoms

The considerations of this final chapter have taught us much, and perhaps more than was to be expected, about things which seem to remain as a last object, at least for the present, for the comprehension of the natural philosopher, viz. about atoms and molecules. We have been able to investigate their shape, measure their size, and estimate their weight; we have also learnt that these small entities exert powerful forces on each other when they come close together. But we have not yet learnt sufficient about their state to be able to solve the puzzle which lies before us in the wonderful property of indivisibility to which atoms owe their name. Indeed, the property of indivisibility seems far more unintelligible than ever, now that we know that the size of atoms is not infinitely small, but is measurable in finite terms. The molecules and atoms concerned in the theory of gases, and more especially with mathematical physics, are small bodies which are only one or more thousand times smaller than the smallest magnitude microscopically visible. We shall scarcely be able to conceive that such large bodies are really indivisible elementary atoms.

We shall be so much the less inclined to this belief as many different reasons can be brought forward for the conclusion that the small particles, named atoms by chemists and physicists, are not monads. The most obvious reason is afforded by the simple relations which show a regular connection[1] between the atomic weights and other properties of the chemical elements conditioned by these atomic weights, and which point to a common origin of all the elements from one and the same substance, as was conjectured by Prout, and after him by Thos. Thomson and Dumas.

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[1] Compare Lothar Meyer, *Die modernen Theorien der Chemie*, section 9, 'Das Wesen der chem. Atome.'

The theory of vortex atoms proposed by Lord Kelvin[1] seems to me to be a happy hypothesis which is well suited to satisfactorily explain the facts; it is directly connected with a similar and rather earlier theory of Rankine's,[2] and with a doctrine taught by Descartes a very long time before. It rests on a mathematical memoir by Helmholtz,[3] in which the vortical motions of a liquid moving without friction are investigated, and especially upon one theorem proved in this memoir respecting vortex lines and vortex filaments. The former name is given by Helmholtz to curved lines which may be so drawn in the liquid that at every point along their whole length they are perpendicular to the direction of the motion of rotation, and are therefore parallel to the axis of rotation; a vortex filament is a thin filament of liquid the axis of which is a vortex line and which is bounded on the outside by a system of vortex lines. Helmholtz proved that, if certain assumptions, satisfied in nature, are made as to the law of action of external forces on the liquid, all the motions so proceed that each vortex line remains permanently made up of the same particles of liquid. Since the vortex lines are in general closed curves, each vortex filament contains a finite and never-changing mass of liquid, which can alter its ring shape and its position, but can never lose the connection of its parts.

Lord Kelvin takes as the foundation of his new theory of atoms the theorem, which this law proves, that the production of new vortices and new vortex filaments would be an act of creation. He considers the so-called atoms to be vortex filaments, and represents them by the smoke-rings which tobacco smokers blow.

However strange this view may appear at first sight, it will be found by everyone who takes the trouble to master it to be well fitted both to represent the facts and also to avoid the philosophical objections which can justly be raised to the assumption of atoms. We may conceive of a substance filling space continuously, and we shall then, in spite of, or even by reason of, this representation, be forced to the assumption that small ring-shaped or even thread-shaped parts separate from the continuous mass which cannot be further divided by any force on earth. These vortices, then, are the atoms of ponderable bodies, and the substance between them remaining unmoved is the ether.

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[1] *Phil. Mag.* 1867 [4] xxxiv. p. 15.

[2] *Ibid.* 1855 [4] x. pp. 354, 411.

[3] Crelle-Borchardt's *Journ. f. Math.* 1858, lv. p. 25.

The unchangeable mass of these *vortex atoms* is determined alone by the states of the motion in which the world was at their creation. The multiplicity of these states has given rise to a multiplicity of kinds of vortex atoms, which, in spite of their multiplicity, were all formed of the same substance and in accordance with the same laws, and which must bear witness to these laws for all time by the regularity of their properties. The conformity to law exhibited by the properties of atoms, and especially the law of the periodicity of these properties, will thus find explanation by this theory.

Lord Kelvin's theory of vortex atoms accounts also for the forces exerted by the atoms on each other. Since the vortex atoms have at once the properties of flexibility and impenetrability, it is not paradoxical to ascribe to them the same kind of elasticity as, on the older wave-theory of light, ether is supposed to possess. We thus understand how easily pendulous motions can pass from the atoms to the ether and from the ether to the atoms, and comprehend how luminous oscillations of the atoms require only vanishingly little energy, as E. Wiedemann has shown.[1]

We may further assume, in respect of atoms of this kind, that they conduct themselves like elastic bodies during an encounter. These atoms can also exert an action at a distance on each other by means of the medium which exists between them but does not share their vortical motions, and yet may transmit pressure; for, as Lord

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[1] Compare §§ 123 and 34.

Kelvin and Tait,[1] Kirchhoff,[2] and Boltzmann[3] have shown in their mathematical papers, rings and other bodies which are in a moving liquid experience an apparent attraction which is comparable with electrodynamic attraction.

All this holds good even if the vortices have not the shape of rings or of unlimited threads. The same forces are also originated by masses, and act between masses which move in different ways. We may therefore also form other similar conceptions of the atoms which correspond better to the views that have been put forward since very old times. Of this nature is the hypothesis of pulsating atoms, which we may look upon as spheres, or bodies of some similar shape, in such a state of motion that regular oscillations, perhaps in the radial direction, go on at every point within them. Bjerknes has mathematically investigated the forces brought into play by such motions, and Schiötz has experimentally examined them.[4]

On both these theories the force exerted by one atom on another would be transmitted by the medium that lies between them without motion and therefore powerless and weightless—the luminiferous ether in fact. The close relations which have been recognised of late years between light and electricity suggest the idea of supposing the forces between the atoms which are transmitted by the ether to be of electrical nature, and of taking the motions inside the atoms, to which the atoms owe their force and nature, to be also of electrical character. These suppositions have often been made, especially by Wiechert[5] and Prince Galitzin.[6]

Each of these theories, whether referring the force between atoms to hydrodynamical motions or to electrical causes, strives after the same end as the kinetic theory of gases; for all these endeavours are aimed at explaining all natural phenomena as the result of motion. If this endeavour is successful we shall have, together with the theory of gases, not only a kinetic theory of liquids and of solids, but also a kinetic theory of atoms and force, of electricity and light.

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[1] *Treatise on Natural Philosophy*, Oxford 1867, i. p. 264; 2nd ed. Cambridge 1879, i. p. 330.

[2] Crelle-Borchardt's *Journal*, 1870, lxxi. pp. 237, 263.

[3] *Ibid.* 1871, lxxiii. p. 111.

[4] *Gött. Nachr.* 1876, Nr. 11; 1877, Nr. 13. F. Auerbach, *Theoret. Hydrodynamik*, 1881.

[5] *Schriften d. phys.-ökon. Ges. zu Königsberg*, 35. Jahrg. 1894; *Sitzungsber.* p. 4; 37. Jahrg. 1896, p. 1.

[6] *Bull. de l'Acad. de St. Petersb.* 1895 [5] iii. p. 1.

# MATHEMATICAL APPENDICES

# APPENDIX I

## *PRESSURE AND ENERGY*

In the first part of this book it has several times been pointed out that we can correctly calculate the pressure exerted by a gas if, instead of ascribing to the molecules, as is actually the case, unequal speeds that are constantly varying, we assume that they have all the same mean speed. This mean value is of such size that the kinetic energy on the assumption of equal speeds in the gas has the same value as it really has with the actual inequalities that exist. The justification of this simplifying assumption rests on the fact that the pressure exerted by a gas is dependent on the speed of the molecules only in so far as it increases in proportion to their kinetic energy.

Against the validity of the reasons marshalled in Chapter II. no objection can be raised. But it will not be superfluous to calculate the pressure without this simplifying assumption. There will therefore be made in the following investigation no assumption of any kind with respect to the distribution of unequal speeds. But the result of the calculation will be the same, viz. that the pressure depends only on the mean kinetic energy.

### 1*. Number of Molecules and their Paths

Let the number of molecules of a gaseous medium in unit volume be $N$. These $N$ molecules do not all move with the same speed, nor even in the same direction; the components $u, v, w$ of the velocity of a molecule, reckoned along three fixed rectangular axes, assume for different molecules values which vary from $-\infty$ to $+\infty$. The number of molecules for which the values of the components differ infinitely little from $u, v, w$, so that they lie between the limits $u$ and $u + du$, $v$ and $v + dv$, $w$ and $w + dw$, is an infinitesimal of the order $du\, dv\, dw$; it may be expressed by

$$NF(u, v, w)du\, dv\, dw,$$

where $F$ denotes a kind of probability-function, with the determination of which we shall proceed in Appendix II. §§ 10*–15*.

Just as the values of the velocity for different particles are in general different, so also will the times be different during which the molecules move in the same direction with unchanged speed. Let the length of this time—that is, of the interval between two successive collisions—be $t$, and let the probability of a molecule's moving for the time $t$ in a straight line with unchanged velocity, whose components are $u, v, w$, and then colliding in the following infinitesimal interval $dt$ be

$$f(t, u, v, w)dt.$$

This function $f$, like the other $F$, I will not here more closely examine, as an obvious property of it is sufficient for our present purpose. Since every path must certainly come to an end, the sum of all the probabilities must be certainty, or

$$\int_0^\infty f(t, u, v, w)dt = 1.$$

With this notation, therefore, the number of molecules in unit volume, which move with the velocities $u, v, w$, but only for the time $t$ without collision, is

$$NF(u, v, w)f(t, u, v, w)dt\,du\,dv\,dw.$$

At the end of time $t$ this group begins a new path in a new direction with a new velocity.

But if we assume that the state of the gas does not change with the time, then for every molecule that at any moment loses the velocity-components $u, v, w$ another molecule must at the same moment gain these velocities as the result of collision. After the interval $t$, therefore, the number of molecules above given move again out of the unit volume under the same circumstances and with the same probability of collision. Thus the number of paths which in the unit of time are newly begun by the $N$ molecules in unit volume with velocities $u, v, w$, and which are ended after time $t$, is

$$NF(u, v, w)f(t, u, v, w)\frac{dt}{t}du\,dv\,dw.$$

## 2*. Summation

We use this formula to determine the number of particles which in a unit of time cross any surface-element within the gas with a given speed in a given direction.

Take the axis of $x$ perpendicular to the plane, and investigate the number of those particles which in a unit of time cross an infinitely small rectangle $dy\,dz$ at the point $(x, y, z)$ with a velocity the components of which are $u, v, w$.

Since this specification of the components determines the direction of the motion of the particles in question, it follows that all these particles must come from a limited region, an oblique parallelopiped in shape, which has the rectangle $dy\,dz$ as base and its length along the direction of motion.

Denote the coordinates of any point in this region relatively to the given point $(x, y, z)$ by $-\mathfrak{x}$, $-\mathfrak{y}$, $-\mathfrak{z}$; these must satisfy the condition

$$\mathfrak{x} : \mathfrak{y} : \mathfrak{z} = u : v : w,$$

and the absolute coordinates of the point are $x - \mathfrak{x}$, $y - \mathfrak{y}$, $z - \mathfrak{z}$. Divide up also this region, from which all the molecules in question come, into infinitely small oblique parallelopipeds

$$d\mathfrak{x}\,d\mathfrak{y}\,d\mathfrak{z} = d\mathfrak{x}\,dy\,dz$$

by planes drawn parallel to that of $yz$.

In one of these volume-elements it will, by § 1*, happen

$$NF(u, v, w)\,f(t, u, v, w)\frac{dt}{t}\,du\,dv\,dw\,d\mathfrak{x}\,dy\,dz$$

times per time-unit that a particle begins a new path, with a velocity whose components are $u, v, w$, in the direction towards the surface-element $dy\,dz$, this path ending after the lapse of time $t$.

The particles will actually reach their mark, the element $dy\,dz$, and pass through it if the time $t$ is sufficient for the path to be traversed, and therefore, in the case of particles moving in the positive direction of $x$, if

$$\mathfrak{x} \not> ut.$$

We consequently obtain the total number of the particles which start from the elements of that oblique parallelopiped standing on the base $dy\,dz$, and pass through the element $dy\,dz$ in unit time with a velocity whose components are $u, v, w$, by summing up the above expression for all the volume-elements with the condition

$$\mathfrak{x} \not> ut,$$

that is, by integrating it with respect to $d\mathfrak{x}$ from the initial value $\mathfrak{x} = 0$ to the limiting value $\mathfrak{x} = ut$. In the second place, to obtain the total number which after a shorter or longer time reach the mark, we have to integrate with respect to $dt$ from $t = 0$ to $t = \infty$. Hence

$$dy\,dz\,du\,dv\,dw\int_0^\infty \frac{dt}{t}\int_0^{ut} d\mathfrak{x} NF(u, v, w) f(t, u, v, w)$$

is the required number of particles which pass through the element $dy\,dz$ in unit time with the velocity whose components are $u, v, w$.

## 3*. Reaction

This formula, however, only gives the number of particles which cross the surface-element from one-half of the medium to the other in the positive direction of $x$, that is, with a velocity such that its component $u$ is positive.

If in like manner we obtain the number of the particles which pass in the reverse direction from the second half of the medium to the first, the value of the relative coordinate $-\mathfrak{x}$, which must be positive since for this motion the component $u$ is negative, must satisfy the condition

$$0 \nless \mathfrak{x} \nless ut.$$

Therefore the number of particles crossing in this opposite direction is

$$dy\,dz\,du\,dv\,dw\int_0^\infty \frac{dt}{t}\int_{ut}^{0} d\mathfrak{x} NF(u, v, w) f(t, u, v, w)$$

$$= -\,dy\,dz\,du\,dv\,dw\int_0^\infty \frac{dt}{t}\int_0^{ut} d\mathfrak{x} NF(u, v, w) f(t, u, v, w).$$

In form this formula is distinguished from the other only by its sign, but if the functions $N, F, f$ depend not only on the given variables $t, u, v, w$, but on the position as well, it may also differ by reason of a difference in the signification of these functions.

## 4*. Summation Carried Out

The integrations can be immediately effected in the case wherein these functions do not depend on position, but when the state of the motion is the same at every point of the gaseous medium. With this assumption we obtain, by aid of a theorem given in § 1*,

$$\pm\, dy\,dz\,du\,dv\,dw\, NF(u, v, w)\int_0^\infty \frac{dt}{t} f(t, u, v, w)\int_0^{ut} d\mathfrak{x}$$

$$= \pm\, NF(u, v, w) u\, du\, dv\, dw\, dy\, dz$$

as the number of particles with the velocities $u, v, w$ which, in a unit of time, cross the surface-element $dy\,dz$ in the interior of the space filled with gas. The upper sign applies to the passage in the positive direction of $x$, and the lower to that in the opposite direction.

The analogous expressions for the other axial directions are

$$\pm\, NF(u, v, w)v\, du\, dv\, dw\, dz\, dx,$$

$$\pm\, NF(u, v, w)w\, du\, dv\, dw\, dx\, dy.$$

These formulæ have a very simple interpretation. For $u\,dy\,dz$ is the volume of an oblique parallelopiped on the base $dy\,dz$, of length equal to the velocity, and of altitude equal to the component $u$; it is thus the volume of the region in which all the particles which cross $dy\,dz$ in a unit of time with the given velocity must have been at the beginning of the time-unit. Since, from the definition of $F$, the first of the three expressions denotes the number of particles in this volume which at any moment are moving with the given velocity, it shows, as do also the other two, that as many particles pass through the surface-element as if none had been previously stopped or deviated.

The motion in a gas which is in the same state of equilibrium at all points of the space occupied by it, therefore, goes on just as if the particles never collided, but moved about in all directions without hindrance.

The reason for this (at first sight) surprising result is simply that, when the requisite state of unchangeable equilibrium is attained, for every particle which loses its motion by collision there occurs another which acquires the same motion by another simultaneous collision.

## 5*. Momentum Carried Over

The possibility thus demonstrated of replacing the hypotheses on which our theory is founded by still simpler assumptions in the case of a gas in equilibrium very considerably facilitates the calculation of the pressure exerted by the gas.

On the theory here assumed, the pressure exerted on a surface within the gaseous medium is measured by the force which one half of the medium exerts on the other from which it is separated by the surface.[1] Since, as has just been proved, the collisions do not come into account in the state of equilibrium, we have to deal only with the force which the particles that pass backwards and forwards over the surface exert in virtue of their own motion, and transmit from one half of the medium to the other. What becomes of this motion after the passage from the one half to the other—whether it is destroyed or transformed—is of no moment, since, in the condition of equilibrium, for every particle that loses its velocity another appears which acquires the same motion by collision.

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[1] See Chap. II. § 12.

We therefore obtain the momentum carried across the surface $dy\,dz$ in the unit of time in the positive direction of $x$ from the first half of the medium into the second by multiplying the above-found number of particles which in unit of time cross the surface with the velocities $u$, $v$, $w$, viz.

$$NF(u, v, w)u\,du\,dv\,dw\,dy\,dz,$$

into the components of the momentum of each of these particles, which are

$$mu,\ mv,\ mw,$$

and then integrating the expressions so obtained. The summations are to be carried out with respect to the possible values of the velocity-components $u$, $v$, $w$, and their limits are determined by noting that the passage from the first half of the medium to the second in the positive direction of $x$ can only occur with such velocities as have a positive component $u$. Consequently, the momenta carried over $dy\,dz$ in unit of time in the positive direction are

$$dy\,dz\,Nm\int_0^\infty du\int_{-\infty}^\infty dv\int_{-\infty}^\infty dw\,u^2F(u, v, w),$$

$$dy\,dz\,Nm\int_0^\infty du\int_{-\infty}^\infty dv\int_{-\infty}^\infty dw\,uvF(u, v, w),$$

$$dy\,dz\,Nm\int_0^\infty du\int_{-\infty}^\infty dv\int_{-\infty}^\infty dw\,uwF(u, v, w).$$

For the particles which pass from the first half to the second, and for the momentum carried with them, the first half is compensated by the passage that occurs in the opposite direction into it from the second half. In this direction the passage can occur only with negative values of $u$; and the number of particles which pass in this direction with velocity-components $u$, $v$, $w$ being

$$-NF(u, v, w)u\,du\,dv\,dw\,dy\,dz,$$

and each carrying with it the momenta $mu$, $mv$, $mw$, the total momenta carried across in the backward direction are

$$-dy\,dz\,Nm\int_{-\infty}^{0}du\int_{-\infty}^{\infty}dv\int_{-\infty}^{\infty}dw\,u^2F(u,v,w),$$

$$-dy\,dz\,Nm\int_{-\infty}^{0}du\int_{-\infty}^{\infty}dv\int_{-\infty}^{\infty}dw\,uvF(u,v,w),$$

$$-dy\,dz\,Nm\int_{-\infty}^{0}du\int_{-\infty}^{\infty}dv\int_{-\infty}^{\infty}dw\,uwF(u,v,w).$$

## 6*. Components of Pressure

The second half of the medium loses these latter momenta and gains the former. The resulting increase of its momentum is, therefore, given by the difference of these expressions, so that

$$dy\,dz\,X_x = dy\,dz\,Nm\int_{-\infty}^{\infty}du\int_{-\infty}^{\infty}dv\int_{-\infty}^{\infty}dw\,u^2F(u,v,w),$$

$$dy\,dz\,Y_x = dy\,dz\,Nm\int_{-\infty}^{\infty}du\int_{-\infty}^{\infty}dv\int_{-\infty}^{\infty}dw\,uvF(u,v,w),$$

$$dy\,dz\,Z_x = dy\,dz\,Nm\int_{-\infty}^{\infty}du\int_{-\infty}^{\infty}dv\int_{-\infty}^{\infty}dw\,uwF(u,v,w)$$

are the components of the momenta which, during the unit of time, pass over the surface $dy\,dz$ from the first half of the medium to the second, or, more briefly, are the components of the force exerted on $dy\,dz$ by the first half towards the second.

Just as we have here found the force-components which act on a surface perpendicular to the $x$-axis, and are denoted by the suffix $x$, we may obtain the analogous magnitudes for the other two axial directions. We thus get, with the corresponding notation, the following values for the forces exerted per unit area, that is, for the pressures,

$$X_x = Nm\int_{-\infty}^{\infty}du\int_{-\infty}^{\infty}dv\int_{-\infty}^{\infty}dw\,u^2F(u,v,w),$$

$$Y_y = Nm\int_{-\infty}^{\infty}du\int_{-\infty}^{\infty}dv\int_{-\infty}^{\infty}dw\,v^2F(u,v,w),$$

$$Z_z = Nm\int_{-\infty}^{\infty}du\int_{-\infty}^{\infty}dv\int_{-\infty}^{\infty}dw\,w^2F(u,v,w),$$

$$Y_z = Z_y = Nm\int_{-\infty}^{\infty}du\int_{-\infty}^{\infty}dv\int_{-\infty}^{\infty}dw\,vwF(u,v,w),$$

$$Z_x = X_z = Nm\int_{-\infty}^{\infty}du\int_{-\infty}^{\infty}dv\int_{-\infty}^{\infty}dw\,wuF(u,v,w),$$

$$X_y = Y_x = Nm\int_{-\infty}^{\infty}du\int_{-\infty}^{\infty}dv\int_{-\infty}^{\infty}dw\,uvF(u,v,w).$$

These formulæ determine the pressure exerted by the half of the medium which is nearer the negative coordinates, and has hitherto been called the first half, on the second, which lies on the positive side. The action of the second half on the first is expressed by the same formulæ with changed sign.

The first three of these six formulæ give the pressures which act normally on the stressed surface, *i.e.* the normal pressures, while the last three express the magnitude of the tangential pressures whose directions lie along the surface itself.

## 7*. Interpretation of the Formulæ

Both forms of pressure are expressed by integrals which, from the meaning of the function $F$, are easily seen to represent probable mean values.

Noting further that

$$Nm = \rho,$$

that is, the mass of gas contained in unit of volume, or its density, we may write the foregoing formulæ thus :—

$$\begin{aligned} X_x &= \rho\,\overline{u^2} & Y_z &= Z_y = \rho\,\overline{vw} \\ Y_y &= \rho\,\overline{v^2} & Z_x &= X_z = \rho\,\overline{wu} \\ Z_z &= \rho\,\overline{w^2} & X_y &= Y_x = \rho\,\overline{uv} \end{aligned}$$

where the bar denotes the mean value of the magnitude placed under it.[1]

These formulæ, which were first given in such generality by Maxwell[2] for the pressure in a gas in any state of motion that does not depend on time or position, can be much simplified when there is only the heat-motion of the molecules and not a forward motion of the gas as a whole. Since in this case the motion is symmetrical in all directions of space, all functions depending on uneven powers of the velocity-components $u$, $v$, $w$ vanish, and therefore

$$\overline{vw} = \overline{wu} = \overline{uv} = 0.$$

These terms also vanish when the direction of motion is along one of the coordinate axes.

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[1] [The author uses the notation $M(x)$ to denote the mean value of $x$, but the ordinary English custom is here followed.—Tr.]

[2] *Phil. Mag.* [4] xxxv. 1868, p. 195.

Further, when the gas has no progressive motion as a whole we shall have

$$\overline{u^2} = \overline{v^2} = \overline{w^2}.$$

The value of these three equal means is easily found; for if $\omega$ is the actual velocity of a particle

$$\omega^2 = u^2 + v^2 + w^2,$$

and therefore $$\overline{\omega^2} = \overline{u^2} + \overline{v^2} + \overline{w^2},$$

and consequently $$\overline{u^2} = \overline{v^2} = \overline{w^2} = \tfrac{1}{3}\overline{\omega^2}.$$

In this special case then

$$X_y = X_z = Y_z = Y_x = Z_x = Z_y = 0,$$
$$X_x = Y_y = Z_z = \tfrac{1}{3}\rho\, \overline{\omega^2};$$

that is, the pressure in a gas which is in equilibrium and at rest as a whole is the same in all directions, and acts always normally to the surface on which it acts.

If the gas possesses a progressive motion in which its whole mass takes part, the magnitudes of the mean values are just as easily found. Let $a$ be the velocity with which the gas as a whole moves in the direction of the component $u$; then, if we put

$$u = u_1 + a,$$

$u_1$ is the component of the molecular motion which is perceptible not as causing change of position, but as producing heat and pressure in the gas, and, by § 33, the relations

$$\overline{u_1{}^2} = \overline{v^2} = \overline{w^2} = \tfrac{1}{3}\overline{\omega_1{}^2}$$

hold good, if we now represent the pure molecular velocity freed from that of the flow by $\omega_1$, where

$$\omega_1{}^2 = u_1{}^2 + v^2 + w^2.$$

We have in this case also, just as before, expressions of the form

$$Y_y = Z_z = \tfrac{1}{3}\rho\, \overline{\omega_1{}^2}$$

for the components of pressure at right angles to the direction of flow. On the contrary, for the pressure in the direction of flow we have

$$X_x = \rho\, \overline{(u_1 + a)^2} = \rho\, \overline{u_1{}^2} + \rho a^2,$$

since $\overline{u_1} = 0$; this is greater than the other components by $\rho a^2$, for we also have

$$\rho\, \overline{u_1}^2 = \tfrac{1}{3}\rho\, \overline{\omega_1}^2.$$

This new magnitude $\rho a^2$ shows itself as the pressure with which the streaming gas strikes against an opposing surface, or, if we consider the reverse direction, the reacting pressure which the issuing stream exerts on the containing vessel (§§ 34, 35). The pressure which the stream of gas exerts normally to its direction of flow, viz.

$$\tfrac{1}{3}\rho\, \overline{\omega_1^2},$$

is smaller than what it would be in the case of rest, viz.

$$\tfrac{1}{3}\rho\, \overline{\omega^2};$$

for in coming to rest the gas retains all its energy, so that the mean value of this energy remains unaltered, or

$$\tfrac{1}{2}\overline{\omega_1}^2 + \tfrac{1}{2}a^2 = \tfrac{1}{2}\overline{\omega^2}.$$

The formula found for the pressure in the case of a gas at rest,

$$p = \tfrac{1}{3}\rho\, \overline{\omega^2},$$

does not differ from that deduced before (§§ 11–13), viz.

$$p = \tfrac{1}{3}\rho G^2,$$

since the magnitude $G$ herein contained denotes the mean value which is determined by the equation

$$G^2 = \overline{\omega^2}.$$

Since this formula gives the pressure $p$ as proportional to the density $\rho$, it expresses Boyle's law.

This deduction of the law is preferable to the former in being as free as possible from unproved hypotheses. We have assumed only that the molecules move in rectilinear paths, and have employed no other hypothesis. *The single assumption, therefore, of rectilinear molecular motion suffices by itself for the proof of Boyle's law.*

Since the sum of the kinetic energy in the unit of volume is

$$K = \tfrac{1}{2}Nm\int_{-\infty}^{\infty} du\int_{-\infty}^{\infty} dv\int_{-\infty}^{\infty} dw\,(u^2 + v^2 + w^2)F(u, v, w)$$
$$= \tfrac{1}{2}\rho\, \overline{\omega^2},$$

we obtain by this method also the known relation (§ 16)

$$p = \tfrac{2}{3}K.$$

If we had taken the molecules to be not all of the same kind, but had assumed that two or more kinds of molecules $m_1$, $m_2$, ... were mixed together, then we should have obtained, both for the transmitted momentum and for the kinetic energy, formulæ of the same form as those just found, but of greater generality. The equations would then have contained summations with respect to all the different molecules $m_1$, $m_2$, ... Instead of the last formula, therefore, we should have obtained, as is obvious without calculation, the equation

$$p_1 + p_2 + \ldots = \tfrac{2}{3}K_1 + \tfrac{2}{3}K_2 + \ldots$$

which has the same meaning as that in § 17, and thus proves Dalton's law for the pressure of mixed gases. *The hypothesis of rectilinear molecular motion therefore is also sufficient by itself for the theoretical proof of Dalton's law.*

## 8*. Kinetic Pressure of Liquefied Substances

It is, perhaps, not even absolutely necessary for the molecular motions to be rectilinear. For Boltzmann[1] has attempted with good results to extend the foregoing considerations to bodies which are in the liquid state, and therefore to substances whose molecules move, not in straight, but in curved paths.

The case is that of substances which are mixed in very great dilution with a liquid; we can imagine, therefore, either a very dilute solution of a solid body, or a liquid which has absorbed small quantities of a gas or contains a small quantity of another liquid. The molecules of the alien body that has been added spread themselves throughout the liquid, and therefore become so widely separated from each other that the forces of cohesion no longer come into play. If we further assume that the liquid also exerts no force on the alien molecules, or that the forces it exerts mutually annul each other, the molecules of the added substance then appear to be quite free from all external forces but that of gravity. They would then move in straight paths just as molecules of gas if they were not hindered by the molecules of the liquid and forced to continually change their direction of motion. Yet they move, and this motion, even if it should happen to be in curved paths, produces a kinetic pressure just as in gases.

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[1] *Zeitschr. für phys. Chem.* vi. 1890, p. 474; vii. 1891, p. 88.

This pressure may be calculated in the same manner as gaseous pressure, and the calculation leads to exactly the same result. If no attractive or repulsive forces act between the molecules of the liquid and of the alien body the particles of the latter move about in the liquid, not in continuously curved paths, but in straight paths like the particles of gas in vacuum. The only difference is this, that the alien particles collide very much oftener in the liquid, and that therefore the free path traversed between successive collisions is very much shorter. But this difference has no influence on the validity of the calculation. There is only a change in signification of the function $f(t, u, v, w)$, which denotes the probability of the path being straight for the interval $t$, to this extent that it has values differing from 0 only for very small values of $t$, and that it vanishes for greater arguments; but thereby no alteration in the final result of the calculation is entailed.

The result is similar in the other case which better corresponds to actuality, viz. when forces do indeed act between the liquid and the alien particles, but when the forces to which a particle is subjected from the molecules of the liquid which surround it mutually balance each other on the average. The path of a particle is then continuously curved, as it is continuously under the action of molecular forces; yet we may look on the path as rectilinear which is traversed during an infinitely small interval of time. To this straight bit of path and to the short time needed for it we have to apply the foregoing calculation, which results in the same value as before for the pressure due to the motion of the added alien particles, and gives the same relation between this kinetic pressure $p$ and the kinetic energy $K$ of the particles contained in unit of volume, viz.

$$p = \tfrac{2}{3}K.$$

This formula remains therefore at least approximately correct when the stretches of which the paths of the molecules are made up are not of finite length. It would therefore be mathematically stricter so to express the condition of its validity that the particles whose motion causes the pressure move under the laws of inertia and collision only, without being subject to external force.

On account of this result Boltzmann's theory of osmotic pressure in liquids is important for the kinetic theory of gases.

Except for this, however, I should not here have mentioned it, since osmotic pressure is not one of the phenomena which the kinetic theory of gases has to explain. I will also not conceal that I do not think van't Hoff's views of the kinetic nature of osmotic pressure to be correct. For osmose does not arise from the kinetic pressure of the dissolved substance, but from quite different forces which cannot be neglected.

At all events, if the formula is to be applied to osmose, it first needs a correction, which G. Elias Müller[1] has pointed out; viz. from the kinetic pressure of the dissolved molecules there must be subtracted the pressure which the displaced particles of liquid would have exerted by their motion. Not till then does it become intelligible that osmose is able to cause a motion of the liquid towards the side of the greater pressure.

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[1] *Theorie der Muskelcontraction*, Leipzig 1891, I. (App.) p. 321.

# APPENDIX II

## *MAXWELL'S LAW*

### 9*. On Some Older Proofs

THE state of equilibrium of a multitude of molecules of gas, as has been already shown in § 22, does not consist in their all moving with equal speed. On the contrary, the velocity of any particle changes at every encounter, not only in direction but also in magnitude. But the values of the speed fluctuate about a mean value. The law of deviation of the actual speeds of the particles from this mean value was first perceived by Maxwell; he found that the components of the molecular velocity are distributed among the particles of a gas in equilibrium with the same regularity as we find in all apparently fortuitous phenomena and processes which are really subject to fixed changes. For the distribution of the speeds the same law holds good which, according to Gauss, regulates the distribution of chance errors of observation among the several observations.

Very many proofs have been given of Maxwell's law. One such proof was attempted in the first edition of this book, wherein the law was put forward as the most probable of all conceivable laws. Although the mathematical investigation of this idea is closely connected with the proof given by Gauss[1] of the method of least squares, the proof in its first form cannot be admitted as valid, and the doubts thrown upon it by Boltzmann[2] and von Kries[3] must be held to be well founded.

N. N. Pirogoff,[4] however, showed that my proof can be justified if the mathematical formulæ are differently interpreted. The differential calculus expresses the property of a function in having a maximum in the same way as its behaviour in maintaining its value when its argument is varied. My formulæ, which I again give in § 12* in unchanged form, need not therefore contain the meaning that Maxwell's law is the most probable of all conceivable laws; but they show, as Boltzmann had already recognised before Pirogoff, that among a *limited* number of molecules the values of the speeds may be distributed in different ways, and that all these different ways possess an *equal* degree of probability. On this theorem Pirogoff founded his proof, which he carried out by the same process as I did mine. Since this altered proof by Pirogoff was originally published in Russian only, and is therefore little known elsewhere, I will here give his method at length.

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[1] *Theoria motus corp. cœl.* §§ 175–177.

[2] *Wiener Sitzungsber.* lxxvi. 1877, p. 373.

[3] *Principien der Wahrscheinlichkeitsrechnung*, Freiburg 1886, Chap. VIII. p. 192.

[4] *Journ. d. Russ. phys.-chem. Ges.* xvii. 1885, pp. 114–135, 281–313. Abstracted in *Fortschr. d. Physik*, 1886, pt. 2, p. 237. *Exner's Repertorium*, xxvii. 1891, p. 540.

Pirogoff starts with the assumption that out of an unlimited number of gaseous molecules, whose motions have already become in accordance with Maxwell's law, a group of $N$ particles is so picked out that the choice is guided only by chance. He then investigates the probability that given values of the velocity-components $u$, $v$, $w$ are to be found in this group. By these values also the average state of the motion of the group, its average speed and energy, are determined. If now a second group of $N$ particles is again picked out by chance, there will be other values of the components in this second group; but the average values of the speed and energy may, in spite of this, be the same as with the first group. The probability that each group will have the same average value is the same for both.

That we may arrive at the formulæ of my former proof by the stricter way suggested by Pirogoff was shown me on February 5, 1882, by Gustav Lübeck, with whom I was then corresponding on the subject of my memoir and his.[1] I had then, unfortunately, no opportunity of making use of this communication. I will therefore now lay the foundation of this proof in a way which will, I hope, be valid as a more comprehensive improvement.

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[1] *Festschrift zur zweiten Säcularfeier des Friedrichswerderschen Gymnasiums in Berlin*, 1881, p. 295; *Ueber die Bewegung eines kugelförmigen Atoms.*

## 10*. Hypotheses Used in the Proof

Maxwell's law of distribution refers to the state which a group of gaseous molecules finally attains as its state of equilibrium in consequence of their encounters. If this state once occurs it is maintained to the last in unchanged fashion. But, strictly speaking, it can only be reached when the number of gaseous molecules is unlimited; for by an encounter any value whatever of velocity may result, and only with an infinite number of particles can all possible values of the speed be actually existing at each moment.

If the number of particles is limited, Maxwell's law must be understood otherwise. Since the state of motion of the group of particles is altered in a perceptible degree at every single encounter between two particles, Maxwell's distribution cannot exist at every moment, but will occur with exactness only when the changing states which succeed each other in the course of a sufficiently long period are all taken into account together. If all these different distributions did not succeed each other, but occurred simultaneously together in an unlimited number of particles, the law would not thereby be changed; but Maxwell's law must be equally valid in both cases.

After this remark we can proceed to investigate more closely the function required which expresses the value of the probability. For this purpose let us consider a large number $Z$, say 1,000 or 100,000, of the changing states succeeding each other, which a group of $N$ particles pass through. On the whole, then, $NZ$ different states of a single particle come into account. Among these numerous cases it will often happen that a given particle $m_1$ attains a velocity the components of which in three rectangular directions are $u_1, v_1, w_1$. The number of cases in which this occurs we may represent by a function of the form

$$NZF(u_1, v_1, w_1);$$

for it must be proportional to the number $NZ$ of states, and it must further depend on the values $u_1, v_1, w_1$ of the components. For $Z = \infty$ the value of the function

$$F_1 \equiv F(u_1, v_1, w_1)$$

which expresses this law of dependence is the probability of occurrence of the possible case that the particle $m_1$ should move with a velocity made up of the components $u_1$, $v_1$, $w_1$.

Although the motion of a particle is not independent of the motions of the other $N-1$ particles, yet the function $F_1$ will be determined only by the three arguments $u_1$, $v_1$, $w_1$ if the $NZF_1$ cases are so counted that account is taken in them only of the state of the one particle $m_1$, and not of the states of the other particles also.

For the same reason, if the particles of the group are all like each other, the probability of the event that a second particle $m_2$ has the components $u_2$, $v_2$, $w_2$ is determined by the same function with different arguments, viz.

$$F_2 \equiv F(u_2, v_2, w_2).$$

From these two values of the probability-function we easily obtain by a known law the expression for the probability of the occurrence of both sets of circumstances, viz. that the particle $m_1$ should have the components $u_1$, $v_1$, $w_1$, and $m_2$ the components $u_2$, $v_2$, $w_2$. It is necessary to assume only that the number $Z$, which we look upon as very large, may be approximately taken as infinitely large, and that the function $F$ is determined in correspondence with this assumption; in this case the two events of $m_1$ possessing the components $u_1$, $v_1$, $w_1$ and of $m_2$ having $u_2$, $v_2$, $w_2$ are independent of each other, and the probability of their simultaneous occurrence is therefore expressed by the product of the two functions, and therefore by[1]

$$F_1 F_2 \equiv F(u_1, v_1, w_1) F(u_2, v_2, w_2).$$

If we also consider a third particle $m_3$ which may have the velocities $u_3$, $v_3$, $w_3$, a fourth with components $u_4$, $v_4$, $w_4$, and so on for all the $N$ particles which form the group, we have in the product of the $N$ factors

$$F_1 F_2 \ldots F_N \equiv F(u_1, v_1, w_1) F(u_2, v_2, w_2) \ldots F(u_N, v_N, w_N)$$

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[1] This formula and those which follow later would contain numerical factors which would have to be formed according to the rules of combinations if we did not fix a definite series of the particles. If we sought the probability that one of two particles $m_1$ and $m_2$ had the components $u_1$, $v_1$, $w_1$, and the other the components $u_2$, $v_2$, $w_2$, this would be twice as great as in the case we have taken. Since these factors have no influence on the result, it would be superfluous to complicate the formulæ by inserting them. The factors, furthermore, disappear when the number of particles considered approximates to infinity. (Encke, *Astron. Jahrb. für* 1834, p. 256.)

the chance of the event that, among all the changing states of the group, the first particle $m_1$ has the components $u_1$, $v_1$, $w_1$, the second $m_2$ the components $u_2$, $v_2$, $w_2$, and so on, the last $m_N$ having the components $u_N$, $v_N$, $w_N$.

In this nothing is assumed regarding the time at which these values of the velocity for the individual particles of the group occur. We may therefore apply the formula to the values of the components which the $N$ particles may have at any given moment whatever.

At another time the particles have different velocities, and $u'_1$, $v'_1$, $w'_1$ may then be the components of $m_1$, also $u'_2$, $v'_2$, $w'_2$ those of $m_2$, &c. The probability of this changed state is then given by the product

$$F'_1 F'_2 \ldots F'_N \equiv F(u'_1, v'_1, w'_1) F(u'_2, v'_2, w'_2) \ldots F(u'_N, v'_N, w'_N),$$

which contains the same function $F$ as the first, but with different arguments.

The two products are equal to each other in value, for each of the states of distribution is as likely as the other, because, according to our supposition, both form part of the state of equilibrium which finally ensues. For equilibrium, therefore, it results that the function $F$ must satisfy the equation

$$F_1 F_2 \ldots F_N = F'_1 F'_2 \ldots F'_N,$$

or that the product

$$F(u_1, v_1, w_1) F(u_2, v_2, w_2) \ldots F(u_N, v_N, w_N)$$

must always have one and the same value for all systems of the values of the variables that occur.[1]

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[1] This theorem is proved differently by Pirogoff (*Journ. d. russ. phys.-chem. Ges.* 1885, xvii.). Pirogoff considers an infinite number of gaseous particles which are in a state of equilibrium. From this infinite multitude $N$ particles are taken out. The probability of finding given values of the components $u$, $v$, $w$ among these $N$ particles is expressed by the given product. Of the same magnitude is the chance of taking a second group of $N$ other particles which, though having different components of velocity from those of the first group, have the same total kinetic energy and the same motion of their centroid. Maxwell's law follows likewise from this assumption.

## 11*. Mechanical Conditions

The correctness of the conclusion that all the states of distribution considered occur with equal probability we see still more clearly when we remember that a change of condition does not occur as a consequence of chance, but that each alteration of the molecular motions takes place in accordance with fixed and invariable mechanical laws. Each distribution of speed that at any moment exists was the necessary consequence of that which preceded it, and from it in its turn necessarily arises a new state with a distribution that is by no means arbitrary, but completely determined.

Before, therefore, the final state, which seems to the observer one of equilibrium, that does not alter with the time, is arrived at in a mass of gas left to itself, the function which expresses the probability of a given value of the speed continually changes its nature according to the fixed laws of mechanics. But when the final state is attained the form of this function remains always the same; only the arguments—the values of the components—then alter at each encounter, this alteration also being subject to the general laws of mechanics. Each system of simultaneous values of the speeds appears therefore as often as that from which it arises and as that which results from it; in other words, the probability of occurrence of all these systems is the same.

The laws from which this conclusion is the necessary consequence are contained in the theorems which deal with the mechanics of systems of free particles in motion. For our problem, the establishment of the law of distribution of the energy and speed, only those theorems come into consideration which contain and determine these magnitudes alone. These theorems are—

1. The principle of the conservation of energy;
2. The principle of the conservation of the motion of the centroid.

Further hypotheses are not needed for the present; indeed both these theorems depend on a single common basis, if we may assume that the action exerted by one particle on another is equal to the reaction which at each moment it experiences itself from the other in the reverse direction.

In respect to the application of these theorems to our proof, only the former, the principle of the conservation of energy, requires a few remarks to be made, since it may be applied in different ways according as the molecules are to be looked on as simple massive points or as made up of atoms. In the former case, of the two kinds of energy, kinetic and potential, the sum of which, according to the principle, possesses a value that is constant for all time and under all circumstances, only the former comes into account; for since two molecules act on each other only at the moment of a collision, the potential energy can be neglected if we take into account in the calculation those speeds with which the particles move *between* two collisions, and not *during* a collision. We have then to consider simply the sum of the kinetic energies as invariable, or to introduce the theorem that no kinetic energy is lost at a collision.

We shall first of all limit our consideration to this simpler case, and postpone that of composite molecules for later investigation in § 21*.

## 12*. Determining Equations

By § 10* our problem consists in finding the function $F(u, v, w)$ which has the property that the product

$$F(u_1, v_1, w_1)F(u_2, v_2, w_2) \dots F(u_N, v_N, w_N)$$

has the same constant value $C$ for all values of the components $u$, $v$, $w$ of the molecular velocities that occur together. According to the last discussion the values of these components are not magnitudes that vary arbitrarily and independently, but they are subject to the conditions that they must satisfy the two named theorems of mechanics. If, then, we denote by $E$ the mean value of the kinetic energy of one of the $N$ molecules in question, by $m$ the mass of a molecule, and finally by $a$, $b$, $c$ the components of the velocity with which the centroid of the whole system of gaseous particles moves, the two theorems are expressed by the equations

$$NE = \tfrac{1}{2}m(u_1^2 + v_1^2 + w_1^2 + u_2^2 + v_2^2 + w_2^2 + \dots + u_N^2 + v_N^2 + w_N^2)$$

$$\left.\begin{aligned} Na &= u_1 + u_2 + \dots + u_N \\ Nb &= v_1 + v_2 + \dots + v_N \\ Nc &= w_1 + w_2 + \dots + w_N \end{aligned}\right\}.$$

For our problem these equations represent the conditions connecting the variable magnitudes $u$, $v$, $w$ with the given constants $E$, $a$, $b$, $c$. We have then from the functional equation

$$C = F(u_1, v_1, w_1)F(u_2, v_2, w_2)\ldots F(u_N, v_N, w_N),$$

coupled with the conditions represented by the above four equations, to determine the function $F(u, v, w)$.

This is done by the known processes of the calculus of variations. If we represent a second system of values which satisfy the equations by the symbols $u_n + \delta u_n$, $v_n + \delta v_n$, $w_n + \delta w_n$, where $n$ may represent any integer between 1 and $N$, then we have also

$$\begin{aligned}
C &= F(u_1 + \delta u_1, v_1 + \delta v_1, w_1 + \delta w_1)\ldots F(u_N + \delta u_N, v_N + \delta v_N, w_N + \delta w_N)\\
NE &= \tfrac{1}{2}m\,\{(u_1 + \delta u_1)^2 + (v_1 + \delta v_1)^2 + (w_1 + \delta w_1)^2 + \ldots\\
&\qquad + (u_N + \delta u_N)^2 + (v_N + \delta v_N)^2 + (w_N + \delta w_N)^2\}\\
Na &= u_1 + \delta u_1 + \ldots + u_N + \delta u_N\\
Nb &= v_1 + \delta v_1 + \ldots + v_N + \delta v_N\\
Nc &= w_1 + \delta w_1 + \ldots + w_N + \delta w_N.
\end{aligned}$$

On subtracting the one system of equations from the other we obtain five equations from which the constants $C$, $E$, $a$, $b$, $c$ are absent. In these equations we take the variations $\delta u$, $\delta v$, $\delta w$ as infinitely small, being justified in this if we choose both systems of values of $u$, $v$, $w$ to be such as to differ infinitely little from each other; developing, then, the equations in powers of $\delta u$, $\delta v$, $\delta w$, and neglecting their higher powers, we obtain five equations whose terms are all of the first order.

If for shortness we put

$$\delta F_n \equiv \frac{dF(u_n, v_n, w_n)}{du_n}\delta u_n + \frac{dF(u_n, v_n, w_n)}{dv_n}\delta v_n + \frac{dF(u_n, v_n, w_n)}{dw_n}\delta w_n,$$

the first equation becomes

$$0 = F_2F_3\ldots F_N\,.\,\delta F_1 + F_1F_3\ldots F_N.\delta F_2 + \ldots + F_1F_2\ldots F_{N-1}\,.\,\delta F_N,$$

which, on dividing by the product of all the functions $F$, we may write in the form

$$0 = \frac{\delta F_1}{F_1} + \frac{\delta F_2}{F_2} + \ldots + \frac{\delta F_N}{F_N}.$$

The single terms of this equation have the meaning

$$\frac{\delta F_n}{F_n} = \frac{1}{F_n}\left(\frac{dF_n}{du_n}\delta u_n + \frac{dF_n}{dv_n}\delta v_n + \frac{dF_n}{dw_n}\delta w_n\right).$$

In addition to this we obtain from the four other equations the simple conditions

$$\begin{aligned} 0 &= u_1\delta u_1 + v_1\delta v_1 + w_1\delta w_1 + \ldots + u_N\delta u_N + v_N\delta v_N + w_N\delta w_N, \\ 0 &= \delta u_1 + \ldots + \delta u_N \\ 0 &= \delta v_1 + \ldots + \delta v_N \\ 0 &= \delta w_1 + \ldots + \delta w_N \end{aligned}$$

to which the variations are subject. The variations are therefore not perfectly arbitrary magnitudes, but are in such wise dependent on each other that four of them are determined by the remaining $3N-4$. The values of these last $3N-4$ are limited only by the condition that they must be infinitely small: for the rest, however, it remains perfectly arbitrary what values we assign to the variations, and what ratios we take between their values. If, therefore, by means of the last four equations we eliminate from the principal equation

$$0 = \frac{\delta F_1}{F_1} + \frac{\delta F_2}{F_2} + \ldots + \frac{\delta F_n}{F_n} + \ldots + \frac{\delta F_N}{F_N}$$

four of the $3N$ variations, we obtain a formula which we can so arrange that its $3N-4$ terms contain each a factor $\delta u$, $\delta v$, $\delta w$ which may have any value whatever. The formula therefore breaks up into $3N-4$ independent equations which do not contain the variations, but only the function $F$ and its arguments.

This elimination is most easily performed by the help of initially undetermined coefficients by which the equations of condition are multiplied before being added to the principal equation: these coefficients, which I will take as $2km$, $-2km\alpha$, $-2km\beta$, $-2km\gamma$, are then so determined that four variations out of the whole disappear; then, by reason of the $3N-4$ other variations being quite arbitrary, their factors are also zero. We thus obtain $3N$ equations of the form

$$\begin{aligned} 0 &= \frac{1}{F_n}\frac{dF_n}{du_n} + 2km(u_n - \alpha) \\ 0 &= \frac{1}{F_n}\frac{dF_n}{dv_n} + 2km(v_n - \beta) \\ 0 &= \frac{1}{F_n}\frac{dF_n}{dw_n} + 2km(w_n - \gamma), \end{aligned}$$

in which for $n$ are to be taken all the integers from 1 to $N$. In all these equations the four magnitudes $k$, $\alpha$, $\beta$, $\gamma$ have each one and the same value, which is therefore a constant independent of $n$ and of $u$, $v$, $w$.

## 13*. Another Method

We may arrive at these formulæ in another, perhaps simpler, way from the functional equation

$$C = F(u_1, v_1, w_1)F(u_2, v_2, w_2) \ldots F(u_N, v_N, w_N),$$

by comparing together two states of the molecular system of which the one immediately follows the other. A change of the state occurs at every collision between two particles: we compare therefore the state of the system before a collision between any two particles with its state immediately after the collision. Of all the particles, then, only those two which collided have changed their motion. We may, then, in the product neglect the factors that have remained unchanged, and thus conclude that

$$F(u_1, v_1, w_1)F(u_2, v_2, w_2) = F(U_1, V_1, W_1)F(U_2, V_2, W_2),$$

if $u_1, v_1, w_1$ and $u_2, v_2, w_2$ are the components of velocity of the two particles before collision, and $U_1, V_1, W_1$ and $U_2, V_2, W_2$ the corresponding values after collision.

We thus arrive at a form of functional equation to which other methods of proof have also led. It first occurs in Maxwell's second[1] proof, and then in the memoirs of Boltzmann,[2] Lorentz,[3] and others. It occurs in these memoirs as expression for the stability of Maxwell's state of distribution: the equation may also be interpreted in such wise that the number of collisions depending on the product $F(u_1, v_1, w_1)F(u_2, v_2, w_2)$, in which the components $u, v, w$ are changed into $U, V, W$, is exactly as great as the number similarly determined by $F(U_1, V_1, W_1)F(U_2, V_2, W_2)$ in which the components $u, v, w$ take the place of the values $U, V, W$.

The functional equation is subject to the conditions

$$\begin{aligned} u_1^2 + v_1^2 + w_1^2 + u_2^2 + v_2^2 + w_2^2 \\ = U_1^2 + V_1^2 + W_1^2 + U_2^2 + V_2^2 + W_2^2 \\ u_1 + u_2 = U_1 + U_2 \\ v_1 + v_2 = V_1 + V_2 \\ w_1 + w_2 = W_1 + W_2 \end{aligned}$$

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[1] *Phil. Trans.* 1866, p. 157; *Scientific Papers*, 1890, ii. p. 45.

[2] *Wiener Sitzungsber.* lviii. 1868, p. 517; lxvi. 1872, p. 275; xcvi. 1887, p. 891; &c.

[3] *Ibid.* xcv. 1887, p. 115.

which express the fact that the collision makes no alteration in either the total kinetic energy or in the motion of the centroid of the two particles.

For the solution we employ in this case too the method of the calculus of variations, which may be here employed without hesitation, as the components are variable magnitudes. But we are also entitled to consider the components $u, v, w$ as variable at the same time that the components $U, V, W$ are constant; in this case we limit our consideration to the cases of collision in which from the original values $u, v, w$ the same values $U, V, W$ always result. We thus obtain the equation

$$0 = F(u_2, v_2, w_2)\delta F(u_1, v_1, w_1) + F(u_1, v_1, w_1)\delta F(u_2, v_2, w_2),$$

or

$$0 = \frac{\delta F(u_1, v_1, w_1)}{F(u_1, v_1, w_1)} + \frac{\delta F(u_2, v_2, w_2)}{F(u_2, v_2, w_2)},$$

in which, as before, is put

$$\delta F(u, v, w) \equiv \frac{dF(u, v, w)}{du}\delta u + \frac{dF(u, v, w)}{dv}\delta v + \frac{dF(u, v, w)}{dw}\delta w;$$

and we have also the conditions

$$\begin{aligned} 0 &= u_1\delta u_1 + v_1\delta v_1 + w_1\delta w_1 + u_2\delta u_2 + v_2\delta v_2 + w_2\delta w_2 \\ 0 &= \delta u_1 + \delta u_2 \\ 0 &= \delta v_1 + \delta v_2 \\ 0 &= \delta w_1 + \delta w_2. \end{aligned}$$

By the former method of elimination we then at once obtain the known equations

$$\begin{aligned} 0 &= \frac{1}{F(u, v, w)}\,\frac{dF(u, v, w)}{du} + 2km(u - \alpha) \\ 0 &= \frac{1}{F(u, v, w)}\,\frac{dF(u, v, w)}{dv} + 2km(v - \beta) \\ 0 &= \frac{1}{F(u, v, w)}\,\frac{dF(u, v, w)}{dw} + 2km(w - \gamma), \end{aligned}$$

in which both $u_1, v_1, w_1$ and $u_2, v_2, w_2$ are to be put for $u, v, w$.

## 14*. Integration of the Equations

The equations we have obtained hold good for all values which we can assume for the components $u_1, v_1, w_1$ or $u_2, v_2, w_2$, or in general $u_n, v_n, w_n$, of the velocity of a molecule. We may then take them as any variable magnitudes we like between the limits

$-\infty$ and $+\infty$. The equations, then, which we may write without the index and in the slightly altered form

$$0=\frac{d\log F}{du}+2km(u-\alpha)$$

$$0=\frac{d\log F}{dv}+2km(v-\beta)$$

$$0=\frac{d\log F}{dw}+2km(w-\gamma),$$

are the differential equations which determine the function $F(u, v, w)$ that depends on the arguments $u, v, w$, and which therefore determine the probability that a molecule moving with the velocities $u, v, w$ occurs in the group in question.

By integration of the equations we obtain

$$F(u, v, w)=Ce^{-km\{(u-\alpha)^2+(v-\beta)^2+(w-\gamma)^2\}},$$

where $e$ is the base of Napierian logarithms and $C$ a constant of integration. Instead of the latter we may introduce another constant $A$ given by the formula

$$C\equiv A\,du\,dv\,dw.$$

We are entitled to make this change, because $du$, $dv$, $dw$ possess constant values as differentials of independently varying magnitudes; considering further that the occurrence of a component of velocity of perfectly definite magnitude—for instance $u$, or, more properly, a value lying between the limits $u$ and $u+du$—can have a probability that is only infinitely small and of the order $du$, we see that $C$ must be an infinitely small magnitude of the order $du\,dv\,dw$. We may therefore understand by $A$ a constant of finite magnitude when we put for the probability-function

$$F(u, v, w)=Ae^{-km\{(u-\alpha)^2+(v-\beta)^2+(w-\gamma)^2\}}\,du\,dv\,dw.$$

This expression exhibits an important property of the function, viz. that it may be broken up into three simpler functions, each of which depends on *one* argument only; for we have

$$F(u, v, w)=U(u)V(v)W(w)du\,dv\,dw,$$

if

$$U(u)\equiv Be^{-km(u-\alpha)^2},$$

$$V(v)\equiv Be^{-km(v-\beta)^2},$$

$$W(w)\equiv Be^{-km(w-\gamma)^2},$$

and

$$B^3\equiv A.$$

This mathematical property of the function $F$ is the expression of the fact that the occurrence of a speed $u$, the probability of which is $U(u)du$, is independent of the values of the simultaneously occurring velocities $v$ and $w$ of the same particle, the probabilities of which are $V(v)dv$ and $W(w)dw$; a fact the correctness of which is so evident of itself that Maxwell chose it as an obvious axiom for the foundation of his first[1] proof of the law found by him.

## 15*. Determination of the Constants

Since the probability that some one of all the conceivably possible values of the speeds may occur is a certainty, and has therefore the value 1, it necessarily follows from the above interpretation of the functions $U$, $V$, $W$ that the sum of the probabilities of all possible values must be 1, or

$$B\int_{-\infty}^{\infty} du\, e^{-km(u-\alpha)^2} = 1,$$

and that for the two other functions two corresponding equations must hold. By simple substitutions all three formulæ give the same result

$$1 = B\int_{-\infty}^{\infty} dr\, e^{-kmr^2} = B\sqrt{(\pi/km)},$$

whereby the constant $B$, and thus the constant of integration $A$, is determined.

We further arrive at a knowledge of the constants $\alpha$, $\beta$, $\gamma$ by calculating the mean values of the components of velocity, or, in other words, as the first equations show, the components $a$, $b$, $c$ of the motion of the centroid. From the equations so obtained,

$$a = B\int_{-\infty}^{\infty} du\, u e^{-km(u-\alpha)^2}$$

$$b = B\int_{-\infty}^{\infty} dv\, v e^{-km(v-\beta)^2}$$

$$c = B\int_{-\infty}^{\infty} dw\, w e^{-km(w-\gamma)^2},$$

we obtain simply

$$\alpha = a,\ \beta = b,\ \gamma = c,$$

since

$$\int_{-\infty}^{\infty} du\, u e^{-km(u-\alpha)^2} \equiv \int_{-\infty}^{\infty} dr(r+\alpha)e^{-kmr^2}$$

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[1] *Phil. Mag.* [4] xix. 1860, p. 22; *Scientific Papers*, i. p. 377.

of which the first term is equal to zero and the second to

$$a\int_{-\infty}^{\infty} dr\, e^{-kmr^2} = a/B.$$

We finally obtain the value of $k$ by calculating the mean value of the kinetic energy of a molecule, which is given by the first equation in § 12*, thus:

$$\begin{aligned}E &= \tfrac{1}{2}Am\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} du\, dv\, dw(u^2 + v^2 + w^2)e^{-km\{(u-a)^2+(v-b)^2+(w-c)^2\}}\\ &= \tfrac{1}{2}Am\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} dr\, ds\, dt\{(r+a)^2 + (s+b)^2 + (t+c)^2\}e^{-km(r^2+s^2+t^2)}\\ &= \frac{3}{4k} + \tfrac{1}{2}m(a^2 + b^2 + c^2).\end{aligned}$$

The meaning of the constant $k$ is, therefore, according to the equation

$$\frac{3}{4k} = E - \tfrac{1}{2}m(a^2 + b^2 + c^2),$$

determined by that part of the kinetic energy which is present in the system independently of its translatory motion as a whole, that is, by the energy of its heat-motion.

## 16*. Law of the Distribution of Speeds

As the values of all the constants in the expression for the probability have been found, we can sum up the result of our investigation in the following way:

In a gas which streams with a velocity whose components are $a$, $b$, $c$, and whose particles are in a state of heat-motion of mean energy $3/4k$ when the equilibrium stage has been reached, out of every $N$ molecules there are

$$n \equiv N(\pi^{-1}km)^{\frac{3}{2}}e^{-km\{(u-a)^2+(v-b)^2+(w-c)^2\}}du\, dv\, dw$$

whose components of velocity lie between the limits $u$ and $u + du$, $v$ and $v + dv$, $w$ and $w + dw$.

If we assume that the gas has no progressive motion as a whole, but possesses only the internal heat-motion in all directions equally and with equal strength, and so put

$$a = b = c = 0,$$

we obtain the simpler expression

$$N(\pi^{-1}km)^{\frac{3}{2}}e^{-km(u^2+v^2+w^2)}du\, dv\, dw$$

for the number of molecules which move with such a velocity and in such a direction that its velocity components are $u, v, w$. Thus, too, the number of particles which have a component $u$, independently of the components $v$ and $w$, which remain undetermined, is

$$N(\pi^{-1}km)^{\frac{1}{2}}e^{-kmu^2}du,$$

and similarly the numbers of particles whose velocities have the components $v$ and $w$ respectively are

$$N(\pi^{-1}km)^{\frac{1}{2}}e^{-kmv^2}dv, \quad N(\pi^{-1}km)^{\frac{1}{2}}e^{-kmw^2}dw.$$

The constant $k$ which here occurs is connected with the mean kinetic energy $E$ of molecular motion by the relation

$$\frac{3}{4k} = E.$$

In these simplified formulæ lies the law found by Maxwell, which has been already pointed out in § 24—the law, that is, that the different values of the components of the molecular velocities are distributed among the molecules considered according to the same rule by which the errors of observation of different magnitudes are distributed among the observations in accordance with the method of calculation by least squares.

According to the formulæ first given, this special case of a gas at rest in space is distinguished from the more general case, in which the gas flows as a whole with a certain velocity, only by the velocity of flow having to be subtracted. The same law holds good when we diminish the components $u, v, w$ of the velocity of a molecule by the components $a, b, c$ of the velocity with which the gas flows as a whole. The molecular motions will therefore not be disturbed by a translatory motion being given to the gas as a whole, but both motions combine simply together.

## 17*. Gas in Rotation

Just as simply stands the matter when the gas is not put into translatory motion, but into rotation about an axis.

In a review of a book[1] Maxwell has pointed out that the general theorems of mechanics mentioned in § 11* are not the only ones which must be taken into account in an exhaustive treatment of the subject. In a system of bodies free from external action, the sum of the energy and the velocity of the centroid of the whole system are not the only invariable magnitudes; but there are others, too, that always have the same value. According to the theorem of the conservation of areas the moments of the momenta of the system about three axes at right angles to each other have also constant values. By the method here employed it is easily possible to take this proposition of mechanics also into account in the calculation.

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[1] Notice of Watson's *Kinetic Theory of Gases*, Oxford 1876, in *Nature* xvi. 1877, p. 242.

If we denote by $x$, $y$, $z$ the rectangular coordinates of a particle of mass $m$ whose velocity is made up of the components $u$, $v$, $w$ in the directions of the system of coordinate axes, this general proposition of mechanics is expressed by the equations

$$\begin{aligned} c_1 &= \Sigma.m(yw - zv) \\ c_2 &= \Sigma.m(zu - xw) \\ c_3 &= \Sigma.m(xv - yu), \end{aligned}$$

in which the magnitudes $c$ are independent of the time and position, and the summations $\Sigma$ are taken over all the particles of the whole mass. We may either refer the coordinates $x$, $y$, $z$ to a fixed system of axes, or choose as origin of coordinates the centroid of the whole gaseous mass, which moves on with unchangeable velocity: we will do the latter in order to gain the advantage of obtaining formulæ which refer only to rotations about the centroid.

The new formulæ differ from those established earlier in § 12* by containing the coordinates as well as the components of velocity, yet they can be introduced as equations of condition in the same way as those which refer to the energy and the motion of the centroid.

For, to express the fact that the occurrence of other values $u + \delta u$, $v + \delta v$, $w + \delta w$ of the velocities has the same degree of probability, provided that they satisfy the laws of mechanics, we have to add to the formulæ before developed the conditions

$$\begin{aligned} c_1 &= \Sigma.m\{y(w + \delta w) - z(v + \delta v)\} \\ c_2 &= \Sigma.m\{z(u + \delta u) - x(w + \delta w)\} \\ c_3 &= \Sigma.m\{x(v + \delta v) - y(u + \delta u)\}\ ; \end{aligned}$$

in these formulæ only the velocities $u$, $v$, $w$, and not the coordinates $x$, $y$, $z$, are varied, since among the changed values

$u + \delta u$, $v + \delta v$, $w + \delta w$ those velocities are to be understood which replace the original values $u$, $v$, $w$ at the same place (and therefore for the same values of $x$, $y$, $z$), but at a different time. From both systems of formulæ it follows that to the equations of condition, to which the variations $\delta u$, $\delta v$, $\delta w$ are subject, must be further added the three equations

$$\begin{aligned} 0 &= \Sigma . m(y\,\delta w - z\,\delta v) \\ 0 &= \Sigma . m(z\,\delta u - x\,\delta w) \\ 0 &= \Sigma . m(x\,\delta v - y\,\delta u). \end{aligned}$$

We take these formulæ into account by multiplying them by three provisionally undetermined but constant factors, which we will denote by $-2k\xi$, $-2k\eta$, $-2k\zeta$, and adding them to the former formulæ, and then the coefficient with which each of the $3N$ variations $\delta u$, $\delta v$, $\delta w$ appears to be multiplied in the sum of the equations is to be put equal to 0.

In this way, instead of the three differential equations that stand at the end of § 12*, we obtain the more general equations

$$\begin{aligned} 0 &= \frac{1}{F}\frac{dF}{du} + 2km(u - \alpha + y\zeta - z\eta) \\ 0 &= \frac{1}{F}\frac{dF}{dv} + 2km(v - \beta + z\xi - x\zeta) \\ 0 &= \frac{1}{F}\frac{dF}{dw} + 2km(w - \gamma + x\eta - y\xi), \end{aligned}$$

which may be integrated when $u$, $v$, $w$ are taken to vary without limit and $x$, $y$, $z$ to be constant.

This integration does not need to be carried out in order to let us see that the result of the calculation will only differ from that in the former case by the magnitudes

$$z\eta - y\zeta, \quad x\zeta - z\xi, \quad y\xi - x\eta$$

having to be subtracted from the variables $u$, $v$, $w$ as well as the constants $\alpha$, $\beta$, $\gamma$. The magnitudes have a similar meaning to those of $\alpha$, $\beta$, $\gamma$. While $\alpha$, $\beta$, $\gamma$ were found equal to the values of the components $a$, $b$, $c$ of the velocity of the centroid, $\xi$, $\eta$, $\zeta$, as it is easy to see, are the values of the angular velocities with which the gaseous mass rotates about the axes of $x$, $y$, $z$; for if this is their interpretation, the sum

$$\alpha + z\eta - y\zeta$$

is the velocity with which a particle at the point $x$, $y$, $z$ advances in the direction of the axis of $x$ while rotating about the axis of $y$ from the $z$-axis to the $x$-axis with the angular velocity $\eta$, and also about the axis of $z$ from the $x$-axis to the $y$-axis with the angular velocity $\zeta$. In exactly similar ways are the two other magnitudes to be interpreted. The formulæ therefore express motions of the gaseous mass which correspond to those of a nut which moves on a screw-spindle that itself moves along and turns about a second axis.

These kinds of motion of the gaseous mass are, as our examination shows, to be simply subtracted from the molecular motion present in order for us to arrive directly at Maxwell's law of distribution for the state of rest. Hence it follows that the individual motions of the molecules are not disturbed if in addition to a forward translatory motion of a gas there are also rotations about any axis in which the gas as a whole takes part. The actual velocities of a particle are thus made up of three parts: firstly, of the motion which the particle would have in accordance with Maxwell's law if the gas were at rest as a whole; secondly, of the velocity with which the centroid of the whole gas moves; and, thirdly, of the motions which it has in taking part in the general rotation with the mean values $\xi$, $\eta$, $\zeta$ of the angular velocities.

Thus the kinetic energy of the molecular motions breaks up into three parts, and the mean energy of a molecule at the point $x$, $y$, $z$ is

$$E = \frac{3}{4k} + \tfrac{1}{2}m\{(a + z\eta - y\zeta)^2 + (b + x\zeta - z\xi)^2 + (c + y\xi - x\eta)^2\}.$$

When the whole amount of energy is known this formula may be used for the determination of the constant $k$.

In order to obtain Maxwell's law of distribution in its simplest form, we have, according to the foregoing discussion, to subtract from the components $u$, $v$, $w$ of the molecular velocity, not always equal values of speed for all the different particles which belong to the system, but for each particle the values of the velocity-components which belong to the whole gas at the point where it actually is. This remark discloses the possibility of widening still further the limits of the region wherein Maxwell's law holds good.

In the simple cases which we have considered the validity of this process would have been easy to see even without mathematical proof; for a gaseous body executes a motion of the centroid and rotations about fixed axes exactly as if it were solid. But if in a gaseous mass there are layers which shift together with unequal velocity or rotate unequally quickly, our formulæ which have been used in the proof are no longer valid with absolute strictness, since the energy within any layer need remain constant as little as any other of the observed magnitudes; for the propositions are only strictly true for the gas as a whole. We may, however, look upon them as approximately valid if the interchange of energy or of velocity between the layers occurs only slowly. With this assumption, which is permissible if the differences in the motion of neighbouring layers are small enough, each of the mechanical theorems remains valid with sufficient exactness even for a single layer within an interval of time that is not too long. At the same time, this interval may be long enough to allow the very rapidly resulting[1] arrangement in the distribution of the velocities according to Maxwell's law to occur. In such cases, therefore, the law must also hold good if the gas is divided into unequally moved layers. In each of these layers, then, Maxwell's law holds good for the distribution of the velocities on this condition, that on each occasion the velocity in which a particle shares by the flow or rotation of its layer is to be subtracted from the value which the particle would have in the state of rest and equilibrium of the gas as a whole.

## 18*. Transformation of Coordinates

In using Maxwell's law it is often of advantage to give it another form by a transformation of coordinates. Naturally it is not always necessary to know how many molecules have a velocity the components of which are $u$, $v$, $w$, that is, a velocity of given magnitude and direction; far oftener the question arises as to the number of particles which possess a given speed, that is, a motion of given magnitude without reference to direction.

This question is answered if we pass over to polar coordinates from the system of rectilinear coordinates to which the components $u$, $v$, $w$ are related, and therefore introduce the absolute velocity

$$\omega = \sqrt{(u^2 + v^2 + w^2)},$$

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[1] Tait, *Trans. Roy. Soc. Edin.* xxxiii. 1886, p. 82; Natanson, *Wied. Ann.* xxxiv. 1888, p. 970.

whose direction is given by the angles $s$ and $\phi$ with reference to a fixed axis, such that

$$u = \omega \cos s,$$
$$v = \omega \sin s \cos \phi,$$
$$w = \omega \sin s \sin \phi.$$

In order not unnecessarily to complicate the calculation, which I wish to carry out without the limiting assumption of a state of rest, I take the position of the coordinate system, which so far has been left arbitrary, such that the axis of $u$, which is also that of the polar system of coordinates, coincides with the direction of the absolute velocity of translation of the whole system

$$o = \sqrt{(a^2 + b^2 + c^2)}.$$

Then in the former formulæ $o$ enters instead of $a$, while $b$ and $c$ vanish altogether. Since, further, the element of volume is now given by the expression $\omega^2 d\omega \sin s \, ds \, d\phi$, we have, instead of the first formula of § 16*, the new one

$$n = N(\pi^{-1}km)^{\frac{3}{2}} e^{-km(\omega^2 - 2\omega o \cos s + o^2)} \omega^2 d\omega \sin s \, ds \, d\phi,$$

and this gives the number of molecules which out of every $N$ move with the velocity $\omega$ in the direction given by $s$ and $\phi$.

From this we obtain by integration the whole number $\nu$ of all those which move with a speed lying between $\omega$ and $\omega + d\omega$, viz.

$$\begin{aligned} \nu &= N(\pi^{-1}km)^{\frac{3}{2}} \omega^2 d\omega \int_0^{2\pi} d\phi \int_0^{\pi} ds \sin s \, e^{-km(\omega^2 - 2\omega o \cos s + o^2)} \\ &= N(\pi^{-1}km)^{\frac{1}{2}} o^{-1} \{e^{-km(\omega - o)^2} - e^{-km(\omega + o)^2}\} \omega d\omega. \end{aligned}$$

With the special assumption that there is no translatory motion, *i.e.* that the gas is at rest as a whole or $o = 0$, this formula, found by Maxwell, becomes

$$\nu = 4N\pi^{-\frac{1}{2}}(km)^{\frac{3}{2}} \omega^2 e^{-km\omega^2} d\omega.$$

This new formula differs from the former formula in § 16* by an important circumstance; while the latter showed a continuous diminution of the probability as the values of the components increased, this has a maximum which occurs for the value

$$km\omega^2 = 1$$

or

$$\omega = (km)^{-\frac{1}{2}} \equiv W.$$

The different values of the absolute speed are separated by this most probable value $W$ in such wise that other values of the speed, whether greater or less, have the less probability the more they differ in value from $W$.

The law of this distribution is graphically represented in § 26 on p. 52. The ordinate of the curve is such that

$$y\,dx = \nu/N,$$

so that it simply denotes the probability of a value $\omega$: the abscissa on the contrary is

$$x = \omega\sqrt{(km)} = \omega/W,$$

and is therefore equal to the ratio of the corresponding value $\omega$ to the most probable value $W$.

## 19*. Mean Values of the Speed and Energy

From the trend of the curve we easily see that the most probable value of the speed is no average value in the usual sense of the words. But the arithmetical mean value $\Omega$ of all the values of the speeds, when each is reckoned according to the frequency of its occurrence, is given by

$$\begin{aligned}\Omega &= 4\pi^{-\frac{1}{2}}(km)^{\frac{3}{2}}\int_0^\infty d\omega\, \omega^3 e^{-km\omega^2}\\ &= 2(\pi km)^{-\frac{1}{2}}.\end{aligned}$$

We may compare with this mean value of the molecular speed that corresponding to the mean energy of a particle in motion

$$E = \tfrac{1}{2}mG^2 = 2\pi^{-\frac{1}{2}}k^{\frac{3}{2}}m^{\frac{5}{2}}\int_0^\infty d\omega\, \omega^4 e^{-km\omega^2} = \frac{3}{4k},$$

which agrees with the formula already found in § 16*, this other mean value $G$ of the molecular speed being therefore given by

$$G = \sqrt{\frac{3}{2km}},$$

the meaning of which is as simple and important as that of the arithmetical mean value $\Omega$. We have in fact to understand by $G$ that speed which all the particles would have if without addition or subtraction of energy the speeds of all were made equal.

Then the simple relation in which these two mean values stand to each other is given by the formula

$$G = \Omega\sqrt{(3\pi/8)} = 1{\cdot}0854\,\Omega$$

which was employed in § 28 to calculate the values of $\Omega$. These magnitudes $G$ and $\Omega$ bear to the most probable value $W$ the ratios given by

$$\tfrac{1}{3}G^2 = \tfrac{1}{8}\pi\Omega^2 = \tfrac{1}{2}W^2;$$

it hence follows that a volume of gas $V$ at the pressure

$$p = \tfrac{1}{3}\rho G^2 = \tfrac{1}{8}\pi\rho\Omega^2,$$

as in § 27, possesses a capacity for doing work equal to

$$pV = \tfrac{1}{2}\rho V W^2,$$

which is as great as its kinetic energy would be if each particle moved with the most probable speed $W$.[1]

A third mean value is also of interest, namely, that which in accordance with the nomenclature adopted by Gauss in the theory of least squares must be termed the *mean probable* value or the value of *mean probability*. This value, which I denote by $O$, is determined by the condition that the cases in which a molecule has a less speed than $O$ occur just as often as those in which the speed of the molecule exceeds the mean value $O$.

Since now the probability of the occurrence of the former case is given by

$$4\pi^{-\frac{1}{2}}(km)^{\frac{3}{2}}\int_0^O d\omega\,\omega^2 e^{-km\varphi^2},$$

and that for the second by

$$4\pi^{-\frac{1}{2}}(km)^{\frac{3}{2}}\int_O^\infty d\omega\,\omega^2 e^{-km\varphi^2},$$

while the sum of both probabilities is

$$4\pi^{-\frac{1}{2}}(km)^{\frac{3}{2}}\int_0^\infty d\omega\,\omega^2 e^{-km\omega^2} = 1,$$

it follows that each of the single probabilities possesses the value $\frac{1}{2}$. The mean probable value $O$ of the molecular speed will therefore be determined by the formula

$$\tfrac{1}{2} = 4\pi^{-\frac{1}{2}}(km)^{\frac{3}{2}}\int_0^O d\omega\,\omega^2 e^{-km\omega^2},$$

or by

$$\tfrac{1}{8}\pi^{\frac{1}{2}} = \int_0^\Psi d\psi\,\psi^2 e^{-\psi^2},$$

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[1] Saalschütz, *Schr. d. phys.-ökon. Ges. zu Königsberg*, 1878, 19. Jahrg., *Sitzungsber.* p. 45

where the upper limit of the integral is

$$\Psi = 2\pi^{-\frac{1}{2}} O/\Omega = O/W.$$

To determine the value of $\Psi$ a numerical evaluation of the above transcendental integral is necessary, which can be carried out by means of different rapidly converging series; and we find

$$\Psi = 1{\cdot}0875,$$

and therefore

$$O = 1{\cdot}0875\, W = 0{\cdot}964\, \Omega.$$

Thus the mean probable value $O$ is greater than the most probable $W$, whereas it is less than the other two mean values, so that the four special values of the molecular speed arranged in order of magnitude form the series[1]

$$W < O < \Omega < G.$$

To exhibit these relationships more clearly some numerical examples calculated from these formulæ have been given in § 28.

We need not here examine more closely the more general case wherein there is also a translatory motion of the gas as a whole in addition to its molecular motion, since the formulæ for the mean energy and the pressure have been already deduced in a more general investigation in § 7*.

## 20*. Mixed Gases

The foregoing investigation may be easily extended to the more general case in which the gaseous medium considered consists of a mixture of different kinds of molecules. The calculation is of exactly the same character, the only difference being that the number of equations of condition is increased.

In order to avoid unnecessary complications let us assume that the gaseous mixture is not in a state of motion as a whole, but, apart from the molecular heat-motions, is at rest and in equilibrium; then for each kind of molecules three equations hold good of the form

$$\begin{array}{lll} 0 = \Sigma.m_1u_1, & 0 = \Sigma.m_1v_1, & 0 = \Sigma.m_1w_1, \\ 0 = \Sigma.m_2u_2, & 0 = \Sigma.m_2v_2, & 0 = \Sigma.m_2w_2, \\ \quad\ldots & \quad\ldots & \quad\ldots \end{array}$$

where $m_1$, $m_2$, . . . denote the masses of the different kinds of molecules, and $u_1, v_1, w_1, u_2, v_2, w_2, \ldots$ the components of their respective velocities. For a mixture of two gases we have therefore six equations to take into account; for a mixture of three gases, nine equations; &c.

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[1] [These means are very approximately as 80 : 87 : 90 : 98 —Tr.].

In addition to these equations, which specially hold for each species separately, there is still a condition relative to the whole number of particles which has to be fulfilled, namely, that the kinetic energy of the whole system shall possess a given value. If we denote by $N_1, N_2, \ldots$ the numbers of particles of each kind, and by $N$ their total number, so that

$$N = N_1 + N_2 + \ldots,$$

and if we further write $E_1, E_2, \ldots$ for the mean values of the energy of a particle of each kind, and $E$ for the mean value for them all, so that

$$NE = N_1 E_1 + N_2 E_2 + \ldots,$$

then

$$NE = \tfrac{1}{2}\Sigma . m_1(u_1{}^2 + v_1{}^2 + w_1{}^2) + \tfrac{1}{2}\Sigma . m_2(u_2{}^2 + v_2{}^2 + w_2{}^2) + \ldots$$

where, as before, $N$ and $E$ are given magnitudes.

If now with respect to this enlarged number of equations of condition we seek the function $F$ which determines the distribution of the different values of the components $u, v, w$ by the same methods of the Calculus of Variations as before in § 12*, there is in the calculation only a difference in the number of the variations that remain arbitrary and of those which are determined by them. The form of the equations therefore remains the same; the number of constants only is increased. For each kind of molecules we obtain differential equations of the form

$$0 = \frac{1}{F}\frac{dF}{du} + 2km(u - \alpha)$$

$$0 = \frac{1}{F}\frac{dF}{dv} + 2km(v - \beta)$$

$$0 = \frac{1}{F}\frac{dF}{dw} + 2km(w - \gamma)$$

as before, wherein $\alpha, \beta, \gamma$ may have different values for different kinds; the constant $k$ however has the same value for all the kinds of molecules, since it is the elimination-coefficient by which the last equation of condition is brought in which takes into account all the particles alike.

If therefore these equations are integrated with the condition that there is no translatory motion but only heat-motions, the same expression

$$(\pi^{-1}km)^{\frac{3}{2}}e^{-km(u^2+v^2+w^2)}du\,dv\,dw$$

results for every gas to represent the probability that its components of velocity have the values $u, v, w$. In this expression the corresponding value of the molecular mass $m$ has to be taken for each kind, while the constant $k$ has the same value for all.

If, as in § 18*, polar coordinates are employed in place of Cartesian, the proposition just shown may be expressed thus, that the probability of a given value $\omega$ of the speed is

$$4\pi^{-\frac{1}{2}}(km)^{\frac{3}{2}}\omega^2e^{-km\omega^2}d\omega$$

for each kind of molecules. Since this expression[1] contains the magnitudes $m$ and $\omega$ only in the combination $m\omega^2$, the simple meaning of the above theorem is that *the probability of a given value of the kinetic energy of a molecule is exactly the same for one component gas as for another.*

From this it follows that the mean value of the kinetic energy of a molecule has the same value for each kind of the molecules, or

$$E_1 = E_2 = \ldots = \frac{3}{4k} = E.$$

Therefore *in a mixture of different gases a state of equilibrium results such that a molecule of each kind possesses on the average the same amount of energy; and the varying values of the energy are distributed among the individual molecules of each kind according to one and the same law of probability, that, namely, which regulates the distribution in unmixed gases also.*

If, therefore, two gases, the molecular motions of which are of equal mean energy, are mixed together, no change in the distribution of the energy occurs. The importance of this theoretical proposition stands out when we compare it with a law obtained by experiment, viz. if two gases of the same temperature are mixed together no change in their temperature occurs. Both laws are identical if, in accordance with the fundamental ideas of this theory, the kinetic energy of the molecular motion is taken as the mechanical measure of the temperature. We are therefore justified, on the ground of this agreement with experiment, in concluding the following law, first established by Clausius (see § 29), and in taking it as definition of equality of temperature, viz. *two different gases are at the same temperature when the mean kinetic energy of the molecules of both kinds is the same.*

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[1] [For it is of the form $4\pi^{-\frac{1}{2}}r^2e^{-r^2}dr$, if $r \equiv km\omega^2$.—Tr.]

If both gases are also under the same pressure, and have therefore equal amounts of kinetic energy in unit volume, the further conclusion of Avogadro's law, discussed in § 31, holds good, viz. that *two different gases at the same temperature and pressure contain in equal volumes equal numbers of molecules.*

## 21*. Polyatomic Molecules

The foregoing considerations can, strictly speaking, claim applicability only to gases whose molecules have no internal motions; for atomic motion was left out of account, and our conclusions are thus justified only for gases whose molecules consist each of a single atom.

For systems of polyatomic molecules the investigation is certainly somewhat more complicated; but for these media too the distribution of the motion among the individual molecules may be found by the same method used before, and also the law of distribution of speeds among the constituents of the molecules, *i.e.* among the atoms.

Let a molecule $m$ consist of a number of similar or different atoms $\mathfrak{m}_1$, $\mathfrak{m}_2$, . . . which, in addition to the molecular velocities $u$, $v$, $w$, execute special atomic motions with the velocities $\mathfrak{u}_1$, $\mathfrak{v}_1$, $\mathfrak{w}_1$, $\mathfrak{u}_2$, $\mathfrak{v}_2$, $\mathfrak{w}_2$, . . . The magnitudes of these last velocities must satisfy the equations

$$0 = \mathbf{S}.\mathfrak{m}\mathfrak{u},\ 0 = \mathbf{S}.\mathfrak{m}\mathfrak{v},\ 0 = \mathbf{S}.\mathfrak{m}\mathfrak{w},$$

when the summation denoted by $\mathbf{S}$ is extended over all the atoms forming a molecule. The equations

$$a\Sigma.m = \Sigma.mu,\ b\Sigma.m = \Sigma.mv,\ c\Sigma.m = \Sigma.mw$$

also hold good, in which $a$, $b$, $c$, as before, denote the velocities of flow of the gas, and the summation $\Sigma$ is extended over all molecules.

But the equation for the kinetic energy takes in this case an essentially different shape. While the motion of the molecules investigated before was not constrained by molecular forces, the new motion of the atoms which now comes in is not free; it takes place under the influence of forces which maintain the combination of the atoms into a molecule, and whose joint effect we call *affinity*. In addition, then, to the kinetic energy, which is made up of the sum of the kinetic energies of the atoms and molecules, we must bring the potential energy also into the theorem, which, therefore, takes the form

$$N(E + \mathfrak{E}) = \tfrac{1}{2}\Sigma.\{m(u^2 + v^2 + w^2) + \mathbf{S}.\mathfrak{m}(\mathfrak{u}^2 + \mathfrak{v}^2 + \mathfrak{w}^2)\} + \Sigma\mathbf{S}.\phi.$$

To the mean energy $E$ of the to-and-fro motion of a molecule, which I will call the *molecular* energy, there is here added on the left-hand side the *atomic* energy $\mathfrak{E}$ which is present inside the molecule, in the form partly of heat-motions of atoms, and partly of chemical affinity, while on the right-hand side these magnitudes are taken into consideration as the kinetic energy of the molecules and atoms, and as chemical work performed by heat. The last magnitude is introduced by a function $\phi$ which represents the part of the work which is done on a single atom contained in the complex of the molecule. So that $\mathbf{S}.\phi$ expresses the amount of chemical work in the molecule, and $\Sigma\mathbf{S}.\phi$ the whole amount of chemical work in the medium.

The value of this chemical energy we may easily express by the attractive forces between the atoms if these forces belong to the class named by Helmholtz *central forces*. Thus, if one atom exerts on another distant by $\mathfrak{r}$ from it a force $\mathfrak{f}(\mathfrak{r})$, the work required to increase this distance by $d\mathfrak{r}$ is

$$\mathfrak{f}(\mathfrak{r})d\mathfrak{r};$$

to overcome the affinity, therefore, in the infinitely small displacement of an atom, an amount of energy or of heat

$$d\phi = \mathbf{S}.\mathfrak{f}(\mathfrak{r})d\mathfrak{r}$$

is used up, so that we find

$$\phi = \mathbf{S}.\int_{\mathfrak{s}}^{\mathfrak{r}} \mathfrak{f}(\mathfrak{r})d\mathfrak{r}$$

as the value of the energy spent, the constant $\mathfrak{s}$ here denoting the smallest distance from the atom in question to which the attracted atom can come.

The new more general formulæ, like the earlier simpler ones, hold good for all possible states of motion, and may therefore undergo variation in the same way as the others. But in this operation we must consider not only the velocities $u, v, w$ of the molecules and the atomic velocities $\mathfrak{u}, \mathfrak{v}, \mathfrak{w}$ as variable, but also the distances $\mathfrak{r}$ and the function $\phi$, since the mode in which the atoms are bound together into molecules and arranged within them is not given. The number of molecules $N$ therefore cannot be taken as absolutely fixed, but we shall have the product

$$N(E + \mathfrak{E}) = H,$$

where $H$ stands for a given constant, which in § 53 was thus denoted.

The variation consequently gives

$$0 = \Sigma.m(u\delta u + v\delta v + w\delta w) + \Sigma\mathsf{S}.\{\mathfrak{m}(\mathfrak{u}\delta\mathfrak{u} + \mathfrak{v}\delta\mathfrak{v} + \mathfrak{w}\delta\mathfrak{w}) + \delta\phi\}$$
$$0 = \Sigma.m\delta u, \; 0 = \Sigma.m\delta v, \; 0 = \Sigma.m\delta w,$$
$$0 = \mathsf{S}.\mathfrak{m}\delta\mathfrak{u}, \; 0 = \mathsf{S}.\mathfrak{m}\delta\mathfrak{v}, \; 0 = \mathsf{S}.\mathfrak{m}\delta\mathfrak{w}.$$

The variation $\delta\phi$ here occurring is not independent of the other variations. For by addition of heat not only does the kinetic energy rise in amount, but also the relaxing of the bonds, which Clausius calls disgregation, increases in continually corresponding measure, till at last it leads to dissociation. The regular connection between these phenomena is to be introduced into the calculation.

Since an increase of the velocity with which the centroid of a molecule moves is conceivable without the internal connection between its component parts needing in any way to be altered, $\phi$ cannot depend on $u, v, w$. On the contrary, $\phi$ must be considered a function of $\mathfrak{u}, \mathfrak{v}, \mathfrak{w}$; for an increase in the atomic motions must cause the distances $\mathfrak{r}$ between the molecules to increase in consequence both of the collisions between the atoms and of their centrifugal force. Hence we must put

$$\delta\phi = \mathsf{S}.\left(\frac{d\phi}{d\mathfrak{u}}\delta\mathfrak{u} + \frac{d\phi}{d\mathfrak{v}}\delta\mathfrak{v} + \frac{d\phi}{d\mathfrak{w}}\delta\mathfrak{w}\right),$$

where the sum is to be taken over all the atoms of the molecule which contains the atom subjected to the influence of affinity.

If now, as before, we denote the probability that an atom possesses the molecular velocities $u, v, w$, and also the special velocities $\mathfrak{u}, \mathfrak{v}, \mathfrak{w}$ by

$$F \equiv F(u, v, w, \mathfrak{u}, \mathfrak{v}, \mathfrak{w}),$$

the formula defining the state of equilibrium of the medium for which we are looking is

$$0 = \Sigma\mathsf{S}.\frac{1}{F}\left(\frac{dF}{du}\delta u + \frac{dF}{dv}\delta v + \frac{dF}{dw}\delta w + \frac{dF}{d\mathfrak{u}}\delta\mathfrak{u} + \frac{dF}{d\mathfrak{v}}\delta\mathfrak{v} + \frac{dF}{d\mathfrak{w}}\delta\mathfrak{w}\right).$$

Since the variations here contained must satisfy the above conditions, we obtain by the method of elimination already used the following differential equations for the determination of the function $F$ :—

$$0 = \frac{1}{F}\frac{dF}{du} + 2km(u - \alpha)$$

$$0 = \frac{1}{F}\frac{dF}{dv} + 2km(v - \beta)$$

$$0 = \frac{1}{F}\frac{dF}{dw} + 2km(w - \gamma)$$

$$0 = \frac{1}{F}\frac{dF}{d\mathfrak{u}} + 2k\left\{\mathfrak{m}(\mathfrak{u} - \mathfrak{a}) + \frac{d\phi}{d\mathfrak{u}}\right\}$$

$$0 = \frac{1}{F}\frac{dF}{d\mathfrak{v}} + 2k\left\{\mathfrak{m}(\mathfrak{v} - \mathfrak{b}) + \frac{d\phi}{d\mathfrak{v}}\right\}$$

$$0 = \frac{1}{F}\frac{dF}{d\mathfrak{w}} + 2k\left\{\mathfrak{m}(\mathfrak{w} - \mathfrak{c}) + \frac{d\phi}{d\mathfrak{w}}\right\}.$$

Here $k$, $\alpha$, $\beta$, $\gamma$ are the same constant magnitudes as before; but $\mathfrak{a}$, $\mathfrak{b}$, $\mathfrak{c}$ are to be considered constant only so far that for all atoms in one and the same molecule they have the same value; they might possibly have different values for different molecules, and, so far at least, should be taken as dependent on the state of the molecule, that is, as functions of $u$, $v$, $w$.

We easily see, however, that the above equations would contradict each other if $\mathfrak{a}$, $\mathfrak{b}$, $\mathfrak{c}$ changed with $u$, $v$, $w$ from molecule to molecule.

By differentiating, for example, the first and fourth of the above equations, we obtain inconsistent values of the second differential coefficient with respect to the two variables $u$, $\mathfrak{u}$, which are independent of each other, thus :—

$$\frac{d^2 \log F}{du\, d\mathfrak{u}} = \frac{d}{d\mathfrak{u}}\left(\frac{1}{F}\frac{dF}{du}\right) = 0$$

$$= \frac{d}{du}\left(\frac{1}{F}\frac{dF}{d\mathfrak{u}}\right) = 2k\mathfrak{m}\frac{d\mathfrak{a}}{du};$$

and similarly with the others; whence we see that the magnitudes $\mathfrak{a}$, $\mathfrak{b}$, $\mathfrak{c}$ must in general be constant in respect to $u$, $v$, $w$ also.

The integration of the equations is now easy to carry out, and we obtain

$$F = Ae^{-k\psi}du\,dv\,dw\,d\mathfrak{u}\,d\mathfrak{v}\,d\mathfrak{w}$$

where

$$\psi \equiv m\{(u-\alpha)^2 + (v-\beta)^2 + (w-\gamma)^2\} \\ + \mathfrak{m}\{(\mathfrak{u}-\mathfrak{a})^2 + (\mathfrak{v}-\mathfrak{b})^2 + (\mathfrak{w}-\mathfrak{c})^2\} + 2\phi,$$

and $A$ denotes a constant which may be different for each kind of atom. This function $F$ may, as before, be broken up into the product of several simple functions, for we may put

$$Ae^{-k\psi} \equiv U(u)V(v)W(w)\mathfrak{F}(\mathfrak{u}, \mathfrak{v}, \mathfrak{w}),$$

of which the first three have the form

$$U(u) \equiv Be^{-km(u-\alpha)^2}$$
$$V(v) \equiv Be^{-km(v-\beta)^2}$$
$$W(w) \equiv Be^{-km(w-\gamma)^2},$$

where by $B$ may be understood a constant which is the same for all molecules and atoms, and the fourth is

$$\mathfrak{F}(\mathfrak{u}, \mathfrak{v}, \mathfrak{w}) \equiv \mathfrak{B}e^{-k\chi}$$

where $\chi \equiv \mathfrak{m}\{(\mathfrak{u}-\mathfrak{a})^2 + (\mathfrak{v}-\mathfrak{b})^2 + (\mathfrak{w}-\mathfrak{c})^2\} + 2\phi$

and $\mathfrak{B}$ denotes a constant which may have a special value for each kind of atoms.

The three former functions have the same meaning as before in § 14*, so that, for instance, $U(u)du$ denotes the probability that the atoms of a molecule move parallel to the $x$-axis with a velocity between $u$ and $u + du$. The determination of the constants can therefore be carried out exactly as before; in this case, too, we have

$$1 = B\int_{-\infty}^{\infty} du\,e^{-km(u-\alpha)^2}$$

$$a = B\int_{-\infty}^{\infty} du\,ue^{-km(u-\alpha)^2}$$

with similar equations for the components $v$ and $w$. Hence follow

$$B = (\pi^{-1}km)^{\frac{1}{2}}$$
$$\alpha = a,\quad \beta = b,\quad \gamma = c.$$

We obtain, therefore, exactly the same equations as before, whence it is proved that *Maxwell's law holds good for composite as well as for simple molecules.*

There finally remains the constant $k$ to determine; as in the special case investigated before, it depends in simple wise on the mean value of the energy.

Since Maxwell's law holds good for polyatomic molecules just as for isolated atoms, the new formulæ also lead to the known value

$$E=\frac{3}{4k}+\tfrac{1}{2}m(a^2+b^2+c^2)$$

for the mean kinetic energy of the centroid of a molecule, and thus, in the special case of a gas in equilibrium and at rest as a whole, to the value

$$E=\frac{3}{4k}.$$

## 22*. Atomic Motions

But another less simple law, which is given by the function $\mathfrak{F}(\mathfrak{u},\mathfrak{v},\mathfrak{w})$, determines the distribution of the internal motions among the atoms composing the molecule. To determine the constants which in the expression of this function have been so far left undetermined, we may in the first place remark that the atoms of one kind have no special motion of translation besides the general motion of the molecules. The mean values, therefore, of the components $\mathfrak{u}$, $\mathfrak{v}$, $\mathfrak{w}$, calculated from the probability-function

$$\mathfrak{B}e^{-k\chi},$$

must all be equal to zero when all the molecules of the whole system are taken into account, and we therefore have

$$\mathfrak{a}=0,\quad \mathfrak{b}=0,\quad \mathfrak{c}=0;$$

for in the integrations with respect to $d\mathfrak{u}$, $d\mathfrak{v}$, $d\mathfrak{w}$ there are as many atoms with negative components $\mathfrak{u}$, $\mathfrak{v}$, $\mathfrak{w}$ as with positive components of the same absolute magnitude, and these atoms are at the same time endowed with the same values $\phi$ of chemical energy; the integral can therefore vanish only if $\mathfrak{a}$, $\mathfrak{b}$, $\mathfrak{c}$ also vanish. We have then more simply

$$\chi=\mathfrak{m}(\mathfrak{u}^2+\mathfrak{v}^2+\mathfrak{w}^2)+2\phi,$$

or $\chi$ is double the total energy, *i.e.* double the sum of the kinetic and potential energies of the atom-complex of a molecule.

In order, further, to find the value of the magnitude $\mathfrak{B}$, a determination is first of all necessary of the limits within which the velocities $\mathfrak{u}$, $\mathfrak{v}$, $\mathfrak{w}$ are variable. These magnitudes cannot assume any value between $-\infty$ and $+\infty$, as in the case of the molecular velocities $u$, $v$, $w$; for if their values were to increase above a certain amount, the energy of the internal motions would be sufficient to break up the combination of the atoms, which would then move on, either singly as independent molecules or in new molecular groupings: the former atomic motions are therefore partly transformed into molecular motions when their value exceeds the limits determined by affinity.

In this view the upper limits of the atomic velocities are determined by the condition that the corresponding kinetic energy of an atom cannot be greater than the energy of affinity which is overcome when the atom considered is to be loosed from the bonds of the molecule. If we denote by $\Phi$ the maximum value of the energy which can be developed by the combination of the atom with the remaining constituents of the molecule, so that

$$\Phi = \mathbf{S}.\int_{\mathfrak{s}}^{\infty} \mathfrak{f}(\mathfrak{r})d\mathfrak{r},$$

then, since the molecule considered is in such a thermal condition and with the disgregation so far advanced that the chemical energy

$$\phi = \mathbf{S}.\int_{\mathfrak{s}}^{\mathfrak{r}} \mathfrak{f}(\mathfrak{r})d\mathfrak{r}$$

has already been overcome by the expansive tendency of heat, there still remains only the difference

$$\Phi - \phi = \mathbf{S}.\int_{\mathfrak{r}}^{\infty} \mathfrak{f}(\mathfrak{r})d\mathfrak{r}$$

to keep the atom in the molecule. The condition, then, which determines the upper limits of the atomic speeds is therefore

$$\tfrac{1}{2}\mathfrak{m}(\mathfrak{u}^2 + \mathfrak{v}^2 + \mathfrak{w}^2) < \Phi - \phi,$$

or, more shortly, with the above definition of $\chi$,

$$\tfrac{1}{2}\chi < \Phi.$$

This equation expresses that the sum of the kinetic and potential energies at any moment within the molecule, or the sum of the heat and chemical affinity within it, must remain smaller than the highest value which the energy of affinity can have; in other cases the stability of the molecule is destroyed.

The value of the constant $\mathfrak{B}$ can therefore be determined by our noting that the sum of the probabilities of all possible cases must be certainty, and that therefore

$$\mathfrak{B}\iiint d\mathfrak{u}\, d\mathfrak{v}\, d\mathfrak{w}\, e^{-k\chi}=1$$

when the limits of the integrations are values connected by the equation

$$\chi=\mathfrak{m}(\mathfrak{u}^2+\mathfrak{v}^2+\mathfrak{w}^2)+2\phi=2\Phi.$$

Without knowing the value of the function $\phi$ we can carry the integration only so far as to express $\mathfrak{B}$ by the transcendental equation

$$1=4\pi\mathfrak{B}\int_0^{\mathfrak{g}} dq\, q^2 e^{-k\chi},$$

where

$$\chi=\mathfrak{m}q^2+2\phi_q,$$

and the limiting value $\mathfrak{g}$ is given by

$$\mathfrak{m}\mathfrak{g}^2+2\phi_{\mathfrak{g}}=2\Phi,$$

$\phi_q$ and $\phi_{\mathfrak{g}}$ being the mean values of $\phi$ corresponding to the velocities $q$ and $\mathfrak{g}$.

We meet the same difficulty in attempting to find that part of the energy which we have called the atomic energy; for, in taking the sum of the kinetic and potential energies within the molecule we obtain on the average

$$\mathfrak{E}=\tfrac{1}{2}\mathfrak{B}\mathsf{S}.\iiint d\mathfrak{u}\, d\mathfrak{v}\, d\mathfrak{w}\, \chi e^{-k\chi},$$

where the limits of the integrations are again conditioned by

$$\tfrac{1}{2}\chi=\tfrac{1}{2}\mathfrak{m}(\mathfrak{u}^2+\mathfrak{v}^2+\mathfrak{w}^2)+\phi=\Phi.$$

Without a knowledge of the function $\phi$ the integration can be carried no further than as is given above for $\mathfrak{B}$.

## 23*. Rotations of the Molecules

It can still be doubted whether the formulæ for the individual motions of the atoms, as they have so far been developed, really contain everything of importance for the nature of the case. If we consider that composite molecules are doubtless thrown into rotation on collision, we must consider our procedure open to suspicion, as in the deduction of the formulæ for composite molecules the theorem of the conservation of areas, which was applied to the case of simple molecules in § 17*, was not regarded. I will therefore take this theorem into account by way of supplement.

According to this theorem the following equations hold for molecules whose mass $m$ is made up of atoms of mass $\mathfrak{m}$, viz.

$$\begin{aligned} c_1 &= \Sigma\mathsf{S}.\mathfrak{m}\{(y+\mathfrak{y})(w+\mathfrak{w}) - (z+\mathfrak{z})(v+\mathfrak{v})\} \\ c_2 &= \Sigma\mathsf{S}.\mathfrak{m}\{(z+\mathfrak{z})(u+\mathfrak{u}) - (x+\mathfrak{x})(w+\mathfrak{w})\} \\ c_3 &= \Sigma\mathsf{S}.\mathfrak{m}\{(x+\mathfrak{x})(v+\mathfrak{v}) - (y+\mathfrak{y})(u+\mathfrak{u})\}, \end{aligned}$$

where $c_1$, $c_2$, $c_3$ are constants, and the summation $\mathsf{S}$ is extended over all the atoms of a molecule, while the summation $\Sigma$ embraces all the molecules of the whole gas; further, by $x$, $y$, $z$ the coordinates of the centroid of a molecule are denoted, and $\mathfrak{x}$, $\mathfrak{y}$, $\mathfrak{z}$ are the coordinates of an atom referred to this centroid as origin. Hence we have the equations

$$\mathsf{S}.\mathfrak{m}\mathfrak{x} = 0, \quad \mathsf{S}.\mathfrak{m}\mathfrak{y} = 0, \quad \mathsf{S}.\mathfrak{m}\mathfrak{z} = 0,$$

and, since we have also

$$\mathsf{S}.\mathfrak{m}\mathfrak{u} = 0, \quad \mathsf{S}.\mathfrak{m}\mathfrak{v} = 0, \quad \mathsf{S}.\mathfrak{m}\mathfrak{w} = 0,$$
$$\mathsf{S}.\mathfrak{m} = m,$$

the equations first given reduce to

$$\begin{aligned} c_1 &= \Sigma.m(yw - zv) + \Sigma\mathsf{S}.\mathfrak{m}(\mathfrak{y}\mathfrak{w} - \mathfrak{z}\mathfrak{v}) \\ c_2 &= \Sigma.m(zu - xw) + \Sigma\mathsf{S}.\mathfrak{m}(\mathfrak{z}\mathfrak{u} - \mathfrak{x}\mathfrak{w}) \\ c_3 &= \Sigma.m(xv - yu) + \Sigma\mathsf{S}.\mathfrak{m}(\mathfrak{x}\mathfrak{v} - \mathfrak{y}\mathfrak{u}). \end{aligned}$$

The two parts into which each sum in this way breaks up are independent of each other. For the second parts, which have still remained double summations, depend only on the position and motion of the atoms inside the molecule, and cannot alter with the velocity and position of the centroid of the molecule, that is, with $u$, $v$, $w$ or $x$, $y$, $z$. If, for instance, to the gas as a whole a constant velocity $u$ were given in the direction of the $x$-axis, or if it were displaced in this direction by a constant amount $x$, such an alteration would be without effect on the processes occurring inside the molecules. Hence it follows that the three equations can only be satisfied if each of the six magnitudes

$$\begin{array}{ll} \Sigma.m(yw - zv) & \qquad \Sigma\mathsf{S}.\mathfrak{m}(\mathfrak{y}\mathfrak{w} - \mathfrak{z}\mathfrak{v}) \\ \Sigma.m(zu - xw) & \qquad \Sigma\mathsf{S}.\mathfrak{m}(\mathfrak{z}\mathfrak{u} - \mathfrak{x}\mathfrak{w}) \\ \Sigma.m(xv - yu) & \qquad \Sigma\mathsf{S}.\mathfrak{m}(\mathfrak{x}\mathfrak{v} - \mathfrak{y}\mathfrak{u}) \end{array}$$

possesses a value that always remains constant.

Hence, in addition to the former equations of condition given in § 21*, we have six new ones of which the first three

$$\begin{aligned} 0 &= \Sigma.m(y\delta w - z\delta v) \\ 0 &= \Sigma.m(z\delta u - x\delta w) \\ 0 &= \Sigma.m(x\delta v - y\delta u) \end{aligned}$$

agree with those already established in § 17* for monatomic molecules. The three others we can write only in the unsimplified form

$$0 = \Sigma \mathsf{S}.\mathfrak{m}\left\{\frac{d(\mathfrak{y}\mathfrak{w} - \mathfrak{z}\mathfrak{v})}{d\mathfrak{u}}\delta\mathfrak{u} + \frac{d(\mathfrak{y}\mathfrak{w} - \mathfrak{z}\mathfrak{v})}{d\mathfrak{v}}\delta\mathfrak{v} + \frac{d(\mathfrak{y}\mathfrak{w} - \mathfrak{z}\mathfrak{v})}{d\mathfrak{w}}\delta\mathfrak{w}\right\}$$

$$0 = \Sigma \mathsf{S}.\mathfrak{m}\left\{\frac{d(\mathfrak{z}\mathfrak{u} - \mathfrak{x}\mathfrak{w})}{d\mathfrak{u}}\delta\mathfrak{u} + \frac{d(\mathfrak{z}\mathfrak{u} - \mathfrak{x}\mathfrak{w})}{d\mathfrak{v}}\delta\mathfrak{v} + \frac{d(\mathfrak{z}\mathfrak{u} - \mathfrak{x}\mathfrak{w})}{d\mathfrak{w}}\delta\mathfrak{w}\right\}$$

$$0 = \Sigma \mathsf{S}.\mathfrak{m}\left\{\frac{d(\mathfrak{x}\mathfrak{v} - \mathfrak{y}\mathfrak{u})}{d\mathfrak{u}}\delta\mathfrak{u} + \frac{d(\mathfrak{x}\mathfrak{v} - \mathfrak{y}\mathfrak{u})}{d\mathfrak{v}}\delta\mathfrak{v} + \frac{d(\mathfrak{x}\mathfrak{v} - \mathfrak{y}\mathfrak{u})}{d\mathfrak{w}}\delta\mathfrak{w}\right\},$$

since we do not know in what way the position given by $\mathfrak{x}$, $\mathfrak{y}$, $\mathfrak{z}$, which an atom has inside the molecule, depends on the components $\mathfrak{u}$, $\mathfrak{v}$, $\mathfrak{w}$ of its velocity.

In order to take account of these conditions we have again to multiply each by a coefficient and then add it to the principal equation, whereupon the resulting equation may be broken up into a number of formulæ. In this way we obtain the equations found already in § 17* for monatomic molecules, viz.

$$0 = \frac{1}{F}\frac{dF}{du} + 2km(u - \alpha + y\zeta - z\eta)$$

$$0 = \frac{1}{F}\frac{dF}{dv} + 2km(v - \beta + z\xi - x\zeta)$$

$$0 = \frac{1}{F}\frac{dF}{dw} + 2km(w - \gamma + x\eta - y\xi),$$

in which $k$, $\alpha$, $\beta$, $\gamma$, $\xi$, $\eta$, $\zeta$ are constants, and also the new equations

$$0 = \frac{1}{F}\frac{dF}{d\mathfrak{u}} + 2km\left\{\mathfrak{m}(\mathfrak{u} - \mathfrak{a}) + \frac{d\phi'}{d\mathfrak{u}}\right\}$$

$$0 = \frac{1}{F}\frac{dF}{d\mathfrak{v}} + 2km\left\{\mathfrak{m}(\mathfrak{v} - \mathfrak{b}) + \frac{d\phi'}{d\mathfrak{v}}\right\}$$

$$0 = \frac{1}{F}\frac{dF}{d\mathfrak{w}} + 2km\left\{\mathfrak{m}(\mathfrak{w} - \mathfrak{c}) + \frac{d\phi'}{d\mathfrak{w}}\right\}$$

in which the function $\phi'$ is connected with the potential energy $\phi$ of the atom by the relation

$$\phi' = \phi + \mathfrak{h}_1(\mathfrak{y}\mathfrak{w} - \mathfrak{z}\mathfrak{v}) + \mathfrak{h}_2(\mathfrak{z}\mathfrak{u} - \mathfrak{x}\mathfrak{w}) + \mathfrak{h}_3(\mathfrak{x}\mathfrak{v} - \mathfrak{y}\mathfrak{u}),$$

and $\mathfrak{a}$, $\mathfrak{b}$, $\mathfrak{c}$, $\mathfrak{h}_1$, $\mathfrak{h}_2$, $\mathfrak{h}_3$ are constant coefficients.

The first three formulæ need not be again investigated. We deduce at once, from their holding good in this case too, that Maxwell's law of distribution in composite molecules also is not disturbed by motions of translation or rotation of the gas as a whole.

If we integrate the last three differential equations we find that the function $F$ contains a factor depending on $\mathfrak{u}$, $\mathfrak{v}$, $\mathfrak{w}$, which may also be brought into the form

$$\mathfrak{B}e^{-k\chi};$$

$\mathfrak{B}$ is here again a constant, and $\chi$ has now the meaning

$$\chi \equiv \mathfrak{m}\{(\mathfrak{u} - \mathfrak{a})^2 + (\mathfrak{v} - \mathfrak{b})^2 + (\mathfrak{w} - \mathfrak{c})^2\} + 2\phi',$$

where $\phi'$ has the value just given.

On the same grounds as those given before in § 22*, all terms drop out of the expression for $\phi'$ which contain uneven powers of $\mathfrak{u}$, $\mathfrak{v}$, $\mathfrak{w}$ or of $\mathfrak{x}$, $\mathfrak{y}$, $\mathfrak{z}$, at least if the supposition is realised that the gas is free from external forces, electrical or magnetic for instance, which cause a definite orientation or a definite direction of rotation of the molecules; for on our supposition each direction is as probable as that which is its exact opposite. Hence it follows that

$$\mathfrak{a} = 0, \quad \mathfrak{b} = 0, \quad \mathfrak{c} = 0,$$
$$\mathfrak{h}_1 = 0, \quad \mathfrak{h}_2 = 0, \quad \mathfrak{h}_3 = 0,$$

so that the function $\chi$ takes again the simple form

$$\chi = \mathfrak{m}(\mathfrak{u}^2 + \mathfrak{v}^2 + \mathfrak{w}^2) + 2\phi,$$

in which $\phi$ denotes the potential energy of the atom $\mathfrak{m}$.

The introduction, therefore, of the theorem of the conservation of areas alters nothing in the result of the calculation; and we may therefore be convinced that, in the formulæ before developed, the energy of the rotatory motion of the molecules has already been taken into account.

The case would, however, be probably different if the gas were dielectrically polarised or encircled by electric currents.

## 24*. Molecular and Atomic Energy

With respect to the formula

$$\mathfrak{E} = \tfrac{1}{2}\mathfrak{B}\mathbf{S}.\iiint d\mathfrak{u}\,d\mathfrak{v}\,d\mathfrak{w}\,\chi e^{-k\chi}$$

thus proved for the whole mean value of the kinetic and potential energy within a molecule, we have already remarked, at the end of § 22*, that the integrations cannot be strictly carried out without a knowledge of the function $\phi$ and of the limits of the integrals which depend on its values.

We may, however, approximately evaluate the triple integral by considering that the functions

$$\tfrac{1}{2}\chi e^{-k\chi} \quad \text{and} \quad \tfrac{1}{2}m\omega^2 e^{-km\omega^2}$$

change value like each other. The values of the integrals of the two functions, if taken between equally wide limits, will therefore be of the same order of magnitude. But the limits extend to infinity in that integral only by means of which the molecular energy $E$ is calculated from the velocity $\omega$, and not in $\mathfrak{E}$, in which the variables $\mathfrak{u}$, $\mathfrak{v}$, $\mathfrak{w}$ are limited by the finite magnitude $\Phi$ in accordance with the equation

$$\tfrac{1}{2}\chi = \tfrac{1}{2}\mathfrak{m}(\mathfrak{u}^2 + \mathfrak{v}^2 + \mathfrak{w}^2) + \phi = \Phi.$$

We may therefore conjecture that integration of the function

$$\tfrac{1}{2}\chi e^{-k\chi}$$

will give a value which is less than $E$. If this conjecture is correct, we may conclude, with due regard to the summation over all the atoms in the molecules indicated in the value of $\mathfrak{E}$ by the sign $\mathbf{S}$, that

$$\mathfrak{E} < \mathfrak{n}E,$$

if $\mathfrak{n}$ denotes the number of atoms combined in the molecule.

If we divide this internal energy of the whole complex of atoms in equal shares among the $\mathfrak{n}$ atoms, each share being

$$\mathfrak{e} \equiv \mathfrak{E}/\mathfrak{n},$$

we may express this conclusion thus, that the mean energy $\mathfrak{e}$ of an atom is less than the energy $E$ of the motion of the centroid of the molecule, or

$$\mathfrak{e} < E.$$

I do not conceal that this conclusion is not proved with convincing force by the foregoing considerations. I will also not suppress the fact that Boltzmann[1] has put forward another law: from reflections that are very similar to those here given, but which seem to me less justifiable, he concludes that the mean energy of an atom $\epsilon$ must be equal in magnitude to the molecular energy $E$. The comparison with experiment, which was instituted in §§ 55, 56, speaks in favour of my view in the great majority of cases.

## 25*. Molecular and Atomic Motion in Mixed Gases

The considerations of the previous paragraphs may without difficulty be extended to gases which, like atmospheric air, contain molecules of different kinds. The more general problem of determining the distribution of the energy between the molecular and atomic motions in such a gaseous mixture depends entirely on the same equations which were established and solved before; we have only in this case to do with a greater number of such equations. We obtain, therefore, for each kind of molecule, and each species of atom, formulæ to express the law of distribution of energy which are quite like the others, and differ from them only in the values of the constants that enter into them.

If, now, we again assume that the mixture considered has no translatory motion, but heat-motion only, and so put

$$a = b = c = 0,$$

the law which determines the energy of molecular motion depends only, as the formulæ of § 21* show, on a single constant $k$, which has the same value for each kind of molecules. It thus follows that the mean value of the energy of molecular motion is the same for each kind of molecules, or

$$E_1 = E_2 = \ldots = \frac{3}{4k} = E.$$

The conclusions drawn from these equalities in § 20* hold good, then, not only for monatomic, but also for polyatomic molecules, so that we are justified in laying down the following laws quite generally, both for chemically simple and chemically compound gases.

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[1] *Wiener Sitzungsber.* lxiii. Abth. 2, 1871, p. 397.

*Two different gases are at the same temperature when the mean energy of the motion of the centroids of the molecules is the same in both gases.*

*If two gases are at the same pressure and temperature, equal volumes of both gases contain equal numbers of molecules.*

The internal motion of the molecules, the atomic motion, does not conform to such simple laws. Since the value of the potential energy, which is spent in the form of chemical affinity when atoms are combined to form molecules, is of different magnitude in different compounds, the value of the energy $\mathfrak{E}$ of the atomic motions inside a molecule is by no means the same for all molecules, but each kind of molecules has a different mean value of this species of energy.

The sums total, therefore, of the energy in two gases at the same pressure and temperature are by no means equal, but only, as stated above, the amounts of the energy of motion of the centroids of the molecules. The correctness of this conclusion is confirmed by experiment, which shows that gases do not in general satisfy the law of Dulong and Petit, and that they therefore possess unequal atomic heats.

# APPENDIX III

## *MOLECULAR FREE PATHS*

### 26*. Probability of a Molecular Free Path of Given Magnitude

THE first calculation of the mean length of the free path of a molecule was given by Clausius,[1] in that memoir which we may rightly consider as the foundation-stone of the theory of gases which rests on the calculus of probabilities. In Chapter VI. I have made the same calculation by another method, as I thought it better to avoid the use of transcendental functions and the methods of the higher analysis. I will here, however, complete that elementary demonstration by treating the problem in Clausius' fashion.

No further assumption respecting the state of motion of the gas and its molecules shall be made than this, that at all places within the gaseous medium the motion goes on in the same way. We may therefore suppose not only that the heat-motion at each point has the same energy, but that at each point it takes place in all directions without distinction, so that every direction of motion has the same probability. Together with this heat-motion we assume a translatory motion of the gas as a whole, but with the limitation that this motion must be regarded as constant within limits of space and time which we shall more closely determine. We may, for example, figure to ourselves the gas as flowing through a pipe.

Within this gas let us consider an arbitrarily chosen molecule, which moves with a given velocity in a given direction. We wish to find the probability that this particle will traverse a path of length $x$ without a collision.

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[1] *Pogg. Ann.* cv. 1858, p. 239; transl. *Phil. Mag.* [4] xvii. 1859, p. 81; *Abhandl. über die mech. Wärmetheorie*, 2. Abth. 1867, p. 260; 2nd ed. iii. 1889–91, p. 46.

If we denote by $a$ the probability that this molecule will traverse a path equal to 1 unhindered, $a$ is a proper fraction which, from the assumption made, is so far of constant magnitude that for every position of the starting-point it has one and the same value. If the gas as a whole has no motion of translation, the value of $a$ is also the same for every direction in which the molecule considered can move.

It therefore follows that the probability of traversing a path equal to 2, that is, the path 1 twice over, is $a.a$ or $a^2$. So, too, the probability of its traversing without collision a path three times as long is $a^3$; and we thus see that in general the probability of an unhindered passage through a length $x$ is given by the function

$$a^x,$$

which we may more conveniently write

$$e^{-x/l},$$

where $e$ is the base of natural logarithms and

$$l \equiv -\frac{1}{\log a},$$

so that, as $a$ is a proper fraction and thus $\log a$ negative, $l$ is positive.

This formula agrees in form and meaning with the expression established in the elementary theory (§ 66), viz.

$$e^{-q},$$

in which $q$ denotes the ratio of the path traversed to the mean free path. We can also now easily see that the constant $l$ means nothing else than the mean probable value of the molecular free path which the molecule considered can attain.

For out of $n$ molecules which move in the same way as the given molecule, that is, with the same velocity and in the same direction, the number

$$ne^{-x/l}$$

traverse the length $x$ without collision, but only

$$ne^{-(x+dx)/l}$$

pass over the length $x + dx$; hence in the length $dx$

$$n\{e^{-x/l} - e^{-(x+dx)/l}\} = ne^{-x/l}\frac{dx}{l}$$

molecules undergo collision from among those that have traversed the path $x$. The sum of all the paths traversed by these molecules amounts to

$$ne^{-x/l}\frac{x}{l}\,dx,$$

and hence as each particle must certainly collide after traversing some distance between the limits $x = 0$ and $x = \infty$, the sum of the paths traversed by all the $n$ molecules before collision is

$$n\int_0^\infty e^{-x/l}\frac{x}{l}\,dx = nl.$$

Thus the mean value of these $n$ free paths is $l$.

This mean probable value of the free path is to be understood as corresponding only to particles that move with a certain definite velocity, since we assumed the same motion for all the $n$ particles; it is therefore denoted by $l$, so as to be different from the symbol $L$ used in § 65. In addition to altering with the speed of the particle, $l$ may in general depend also on position, time, and direction, if the molecular motion of the gas alters with these magnitudes.

## 27*. Probability of an Encounter

Before we determine the value of the free path $l$ for a particle of a real gas, let us solve, by Clausius' method, a preliminary problem.

Into a space filled with molecules at rest, of which $n$ are contained in each unit of volume, let a molecule enter with the velocity $\omega$. What is the probability that this molecule may in a given interval $t$, say the unit of time, collide with one of those at rest, the radius of the sphere of action being $\varsigma$?

In the time $t$ the molecule traverses the length $\omega t$; its sphere of action therefore moves through the volume $\pi\varsigma^2\omega t$. Since in this space there are $\pi n\varsigma^2\omega t$ molecules at rest, the probable number of encounters which the molecule meets with in the interval $t$ is also

$$\pi n\varsigma^2\omega t,$$

and the probable number of encounters in unit time is therefore given by the product

$$\pi n\varsigma^2\omega,$$

the value of which may also be interpreted as the probability of an encounter in unit time.

To this simple problem another, which better corresponds to reality, may be reduced.

Suppose a multitude of particles in motion, and all with the same velocity in the same direction, so that all the particles have the same velocity-components $U, V, W$; assume further that the particles fill the space with equal density on the average, and that there are $n$ of these particles per unit volume. Into this swarm let another, or even a number of other particles, enter, which move with a different velocity in a different direction; let the velocity of this second group when resolved in the same three directions have the components $u, v, w$. We have to find the probability of an encounter, and the probable time that elapses before an encounter occurs.

The probability of an encounter in this case is the same as if, instead of allowing both systems to move in two different directions, we had, more simply, assumed that the one swarm was at rest and the other moved relatively to it with the relative velocity

$$r = \sqrt{\{(u-U)^2 + (v-V)^2 + (w-W)^2\}}.$$

The probability, therefore, that a given particle of the one system should collide with any particle of the other in the unit of time is to be represented by the same formula as before when for the absolute velocity $\omega$ the relative velocity $r$ is substituted. Thus the probability sought is

$$\pi n s^2 r.$$

## 28*. Number of Encounters

From this simple formula we obtain that which holds for the case of a real gas by simply finding the mean value of the relative velocity of two of its molecules. In this calculation we first of all assume that all the particles are moving with the same speed. This assumption is certainly not quite true, as we know from our former investigations; since, however, it has shown itself very serviceable in the calculation of the pressure and in other problems, we may here, too, expect by its help to obtain formulæ that are approximately correct.

If, as before, we denote by $G$ the velocity which all the molecules possess, the components into which the velocity of any particle can be resolved are expressed by the formulæ

$$U = G \cos s$$
$$V = G \sin s \cos \phi$$
$$W = G \sin s \sin \phi,$$

in which $s$ and $\phi$ denote two angles which determine the direction of the motion. By formulæ of the same kind we may express the velocity-components $u$, $v$, $w$ of the particle whose collisions with others we wish to count; but these formulæ are substantially simplified if we so choose the system of coordinates that one of the three axes coincides with the direction of motion of this molecule. We may therefore put

$$u = G, \quad v = 0, \quad w = 0,$$

and the relative velocity of this particle with respect to the other taken is

$$r = G\sqrt{(2 - 2 \cos s)} = 2G \sin \tfrac{1}{2}s.$$

On substitution, then, we get

$$\pi n s^2 r = 2\pi n s^2 G \sin \tfrac{1}{2}s,$$

and this magnitude denotes the number of particles with which in unit time any particle so collides that the directions of motion of the colliding particles make the angle $s$ with each other.

In order to calculate the total number of collisions which a particle suffers in the unit of time we have to take the sum of the values of the above expression for all values of the angles $s$. It is therefore necessary to know how great is the number $n$ of the particles for which the angle of encounter with the particle considered has the value $s$, or, better expressed, a value differing infinitely little from $s$, so as to lie between $s$ and $s + ds$ as its limits. We find this number by making use of the property of heat-motion, that it goes on in the same way in all directions without distinction, so that equal numbers of particles move in every direction.

Consider all the particles with their directions of motion to be so displaced—the latter parallel to themselves—that all move towards the colliding molecule, which for the instant is considered at rest; then the paths of all the particles which make an angle between $s$ and $s + ds$ with the colliding particle fall in the space included between two infinitely close cones whose vertices lie on the colliding particle and whose axes coincide with the direction of its motion. The number of particles with a given direction, therefore, when all directions occur equally, bears the same ratio to the whole number of particles as the surface of the zone intercepted between these two cones on a sphere constructed with the colliding molecule as centre bears to the whole surface of the sphere, viz.

$$2\pi \sin s\, ds : 4\pi.$$

The number, therefore, $n$ of the particles in the unit of volume which move in the direction defined by the angle $s$ is

$$n = \tfrac{1}{2} N \sin s\, ds,$$

where $N$ is the whole number contained in unit volume.

It is now easy to find, in the way required above, the total number of the collisions. Since the angle $s$ can increase from 0° to 180°, the value of this sum is

$$\mathrm{A} = \pi \mathrm{s}^2 NG \int_0^\pi \sin \tfrac{1}{2}s \sin s\, ds = 2\pi \mathrm{s}^2 NG \int_0^\pi \sin^2 \tfrac{1}{2}s \cos \tfrac{1}{2}s\, ds\,;$$

and the evaluation of this integral gives the value

$$\mathrm{A} = \tfrac{4}{3}\pi \mathrm{s}^2 NG$$

for the number of collisions which a particle undergoes in unit time in a large group of other similar particles, when all the particles have the same velocity $G$, and there are on the average $N$ particles in unit volume.

Compare this number with that first found

$$\pi \mathrm{s}^2 n\omega,$$

which holds for the case of a particle when it moves with the speed $\omega$ among a multitude of particles at rest, of which there are $n$ in the unit of volume. If we assume the speed and the number of particles to be the same in both cases, or $\omega = G$ and $n = N$, we see that the number of collisions denoted by A is greater than the other in the ratio 4 : 3. A gaseous particle, therefore, as Clausius[1] first perceived, meets with others more frequently when they are all in motion than when one only is in motion and the others are at rest.

Inversely, the mean length of the straight path which a particle traverses between two successive collisions is smaller in the case when all the particles are in motion than in the other. The value of this free path is simply found by dividing the whole distance travelled in the unit of time (which is measured by the velocity) by the number of collisions experienced in the same time. We thus obtain

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[1] *Phil. Mag.* [4] xix. 1860, p. 434; *Abhandl. über die mech. Wärmetheorie*, 2. Abth. 1867, Note on p. 265.

$$\frac{\omega}{\pi n s^2 \omega} = \frac{1}{\pi n s^2}$$

for the value of the free path of a particle in a swarm of particles at rest, but

$$\frac{G}{\mathrm{A}} = \frac{3}{4\pi N s^2}$$

for its value in a swarm of particles in motion. This calculation shows the correctness of the value given in Chapter VI. § 67 for the ratio of the free paths in the two cases.

## 29*. Mean Collision-frequency according to Maxwell's Law

The assumption that all the particles possess equal velocities is not, however, strictly true: we should rather take Maxwell's law, proved in Appendix II., according to which, if there are $N$ molecules of a gas in unit volume and the gas has no progressive motion, the number of them with velocity-components $U$, $V$, $W$ is

$$n = N(km/\pi)^{\frac{3}{2}} e^{-km(U^2+V^2+W^2)} dU\,dV\,dW.$$

Introducing this value of $n$ into the formula (§ 27*)

$$\pi n s^2 r = \pi n s^2 \sqrt{\{(u-U)^2 + (v-V)^2 + (w-W)^2\}},$$

which gives the frequency of collision of a particle, whose velocity-components are $u, v, w$, with $n$ others which move about in unit volume with velocity-components $U$, $V$, $W$, and integrating we obtain

$$\mathrm{B} = \pi s^2 N \left(\frac{km}{\pi}\right)^{\frac{3}{2}} \int_{-\infty}^{\infty} dU \int_{-\infty}^{\infty} dV \int_{-\infty}^{\infty} dW\, r e^{-km(U^2+V^2+W^2)}$$

for the number of collisions which a particle with velocity-components $u, v, w$ makes in one second with all the $N$ molecules contained in unit volume. Since

$$r = \sqrt{\{(u-U)^2 + (v-V)^2 + (w-W)^2\}},$$

this value B depends on $u, v, w$, and consequently on the velocity $\omega = \sqrt{(u^2 + v^2 + w^2)}$ with which the particle in question moves.

Let us first of all investigate, not this value B, but the average value Γ of the collision-frequencies of all possible particles. For this we remark that the probability of the occurrence of the components $u$, $v$, $w$ is expressed by

$$\nu = (km/\pi)^{\frac{3}{2}} e^{-km(u^2+v^2+w^2)} du\, dv\, dw.$$

We then obtain the probable average value of B by multiplying it by $\nu$ and then integrating with respect to $u$, $v$, $w$ between the limits $-\infty$ and $\infty$. The average value of the frequency of collision of any particle whatever is therefore, according to Maxwell's law, given by

$$\Gamma = \pi s^2 N (km/\pi)^3 \int_{-\infty}^{\infty} du \int_{-\infty}^{\infty} dv \int_{-\infty}^{\infty} dw \int_{-\infty}^{\infty} dU \int_{-\infty}^{\infty} dV \int_{-\infty}^{\infty} dW\, r e^{-\phi}$$

where $r$ and $\phi$ are connected with the variables of integration by the relations

$$r = \sqrt{\{(u-U)^2 + (v-V)^2 + (w-W)^2\}}$$
$$\phi = km(u^2 + v^2 + w^2 + U^2 + V^2 + W^2).$$

This sextuple integration assumes a much simpler form with the substitutions

$$\begin{aligned} u &\equiv \mathfrak{U} + \tfrac{1}{2}\mathfrak{u} & U &\equiv \mathfrak{U} - \tfrac{1}{2}\mathfrak{u} \\ v &\equiv \mathfrak{V} + \tfrac{1}{2}\mathfrak{v} & V &\equiv \mathfrak{V} - \tfrac{1}{2}\mathfrak{v} \\ w &\equiv \mathfrak{W} + \tfrac{1}{2}\mathfrak{w} & W &\equiv \mathfrak{W} - \tfrac{1}{2}\mathfrak{w}, \end{aligned}$$

for then

$$r = \sqrt{(\mathfrak{u}^2 + \mathfrak{v}^2 + \mathfrak{w}^2)}$$

$$\phi = 2km(\mathfrak{U}^2 + \mathfrak{V}^2 + \mathfrak{W}^2) + \tfrac{1}{2}km(\mathfrak{u}^2 + \mathfrak{v}^2 + \mathfrak{w}^2),$$

and therefore Γ takes the form

$$\Gamma = \pi s^2 N (km/\pi)^3 PQ$$

of a product of two triple integrals

$$P = \int_{-\infty}^{\infty} d\mathfrak{U} \int_{-\infty}^{\infty} d\mathfrak{V} \int_{-\infty}^{\infty} d\mathfrak{W}\, e^{-2km(\mathfrak{U}^2 + \mathfrak{V}^2 + \mathfrak{W}^2)}$$

$$Q = \int_{-\infty}^{\infty} d\mathfrak{u} \int_{-\infty}^{\infty} d\mathfrak{v} \int_{-\infty}^{\infty} d\mathfrak{w} \sqrt{(\mathfrak{u}^2 + \mathfrak{v}^2 + \mathfrak{w}^2)}\, e^{-\frac{1}{2}km(\mathfrak{u}^2 + \mathfrak{v}^2 + \mathfrak{w}^2)},$$

which can be easily evaluated; for $P$ consists of three factors, of which each is a simple integral of the form

$$\int_{-\infty}^{\infty} d\mathfrak{U}\, e^{-2km\mathfrak{U}^2} = \sqrt{(\pi/2km)};$$

and on introducing polar coordinates as given by

$$\mathfrak{u} = \omega \cos s, \quad \mathfrak{v} = \omega \sin s \cos \psi, \quad \mathfrak{w} = \omega \sin s \sin \psi$$

$Q$ takes the simple form

$$Q = \int_0^{2\pi} d\psi \int_0^{\pi} ds \sin s \int_0^{\infty} d\omega\, \omega^3 e^{-\frac{1}{2}km\omega^2},$$

which leads to the value

$$Q = 8\pi / k^2 m^2.$$

Hence, finally, we find for the average number of collisions which a particle undergoes in unit time

$$\Gamma = 2N\mathfrak{s}^2 \surd(2\pi / km),$$

or, if the mean velocity $\Omega$ of the molecular motion as calculated in § 19* is introduced,

$$\Gamma = \surd 2\pi\mathfrak{s}^2 N\Omega.$$

This formula, first given by Maxwell,[1] differs from that of Clausius, which was deduced in § 28*, only in the slightly different factor $\surd 2 \equiv 1{\cdot}41$ instead of $\frac{4}{3} \equiv 1{\cdot}33$. The assumption, therefore, which is not quite correct, that a single mean velocity may be ascribed to all the particles instead of velocities that are constantly changing, leads in this problem, too, to tolerably correct conclusions.

## 30*. Collision-frequency in Mixed Gases

This procedure may be also extended to the case of two different gases mixed together, as of nitrogen and oxygen in atmospheric air. If we wish to determine the collision-frequency of a particle of gas in such a mixture, we have only to note that this is made up of two parts, viz. the collision-frequency with particles of its own kind and the collision-frequency with particles of the other sort. The former number is given by the calculation just made; the latter can be obtained by repeating that calculation, and remembering that the molecules of the two kinds of gas differ not only in mass, but also in the magnitude of their sphere of action, so that unit volume of the mixture may contain unequal numbers of them. We must therefore distinguish the different values of $m$, $\mathfrak{s}$, and $N$; on the contrary the value of the constant

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[1] *Phil. Mag.* [4] xix. 1860, p. 28; *Scientific Papers* (Cambridge 1890), i. p. 387.

$k$ must be taken the same for both kinds of gases, since they are at the same temperature.

The calculation is, however, no more difficult if we do not introduce the last condition, but take $k$ too as different for the two gases. This generalisation is further not without advantage, but will be of importance in the calculation of the conductivity for heat. In a gas in which the temperature alters from place to place layers of different temperatures come into contact. The free path of a particle will therefore depend not only on the temperature of the layer from which it proceeds, but also on the temperature of the layers into which it enters. In order to be able to apply our calculation to this process also, which we shall investigate later on, we assume the values of the magnitude $k$ for the two kinds of gaseous particles to be different.

Let $m_1$ and $m_2$ be the molecular weights of the two sorts of particles, $u_1$, $v_1$, and $w_1$ the velocity-components of a molecule $m_1$, and $u_2$, $v_2$, $w_2$ the velocity-components of a molecule $m_2$; also let $N_1$ and $N_2$ denote the number of molecules of each kind contained in unit volume, $k_1$ and $k_2$ the values of the constants which determine the temperatures of the two gases, $\Omega_1$ and $\Omega_2$ the mean values of the molecular speeds which are given by the relations

$$\Omega_1 = 2/\sqrt{(\pi k_1 m_1)},\quad \Omega_2 = 2/\sqrt{(\pi k_2 m_2)}\,;$$

finally, let $s_1$, $s_2$, and $\sigma$ be the radii of the spheres of action or the distances within which two molecules $m_1$, two molecules $m_2$, or a molecule $m_1$ and a molecule $m_2$, approach each other during collision. Then the mean number of collisions $\Gamma_1$ experienced by a molecule $m_1$ in unit time, and the mean number $\Gamma_2$ for a molecule $m_2$ have the values

$$\Gamma_1 = \sqrt{2}\pi s_1{}^2 N_1 \Omega_1 + \pi\sigma^2 N_2 \gamma$$
$$\Gamma_2 = \sqrt{2}\pi s_2{}^2 N_2 \Omega_2 + \pi\sigma^2 N_1 \gamma,$$

in which the first terms are formed in accordance with the formula of § 29*; in the last terms, which represent in each case the number of collisions with molecules of the other kind, $\gamma$ is given by

$$\gamma = (\pi^{-1} k_1 m_1 \,.\, \pi^{-1} k_2 m_2)^{\frac{3}{2}} \int_{-\infty}^{\infty} du_1 \int_{-\infty}^{\infty} dv_1 \int_{-\infty}^{\infty} dw_1 \int_{-\infty}^{\infty} du_2 \int_{-\infty}^{\infty} dv_2 \int_{-\infty}^{\infty} dw_2\, r e^{-\phi}$$

where

$$r = \sqrt{\{(u_1 - u_2)^2 + (v_1 - v_2)^2 + (w_1 - w_2)^2\}}$$
$$\phi = k_1 m_1 (u_1{}^2 + v_1{}^2 + w_1{}^2) + k_2 m_2 (u_2{}^2 + v_2{}^2 + w_2{}^2).$$

To simplify this integral put, in like fashion as in the former case,

$$u_1 \equiv \mathfrak{U} + \frac{k_2m_2}{k_1m_1 + k_2m_2}\mathfrak{u} \qquad u_2 \equiv \mathfrak{U} - \frac{k_1m_1}{k_1m_1 + k_2m_2}\mathfrak{u}$$

$$v_1 \equiv \mathfrak{V} + \frac{k_2m_2}{k_1m_1 + k_2m_2}\mathfrak{v} \qquad v_2 \equiv \mathfrak{V} - \frac{k_1m_1}{k_1m_1 + k_2m_2}\mathfrak{v}$$

$$w_1 \equiv \mathfrak{W} + \frac{k_2m_2}{k_1m_1 + k_2m_2}\mathfrak{w} \qquad w_2 \equiv \mathfrak{W} - \frac{k_1m_1}{k_1m_1 + k_2m_2}\mathfrak{w}.$$

Then

$$r = \sqrt{(\mathfrak{u}^2 + \mathfrak{v}^2 + \mathfrak{w}^2)}$$

$$\phi = (k_1m_1 + k_2m_2)(\mathfrak{U}^2 + \mathfrak{V}^2 + \mathfrak{W}^2) + \frac{k_1m_1k_2m_2}{k_1m_1 + k_2m_2}(\mathfrak{u}^2 + \mathfrak{v}^2 + \mathfrak{w}^2),$$

and by evaluation of the sextuple integral

$$\gamma = (\pi^{-1}k_1m_1 \,.\, \pi^{-1}k_2m_2)^{\frac{3}{2}}\int_{-\infty}^{\infty} d\mathfrak{u}\int_{-\infty}^{\infty} d\mathfrak{v}\int_{-\infty}^{\infty} r\,d\mathfrak{w}\int_{-\infty}^{\infty} d\mathfrak{U}\int_{-\infty}^{\infty} d\mathfrak{V}\int_{-\infty}^{\infty} d\mathfrak{W}\,e^{-\phi}$$

we obtain

$$\gamma = 2\sqrt{\left(\frac{k_1m_1 + k_2m_2}{\pi k_1m_1k_2m_2}\right)},$$

or, on substitution of the mean values of the molecular speeds,

$$\gamma = \sqrt{(\Omega_1{}^2 + \Omega_2{}^2)}.$$

Finally, then, the collision-frequencies of the particles of the two kinds are given by

$$\Gamma_1 = \sqrt{2}\pi s_1{}^2N_1\Omega_1 + \pi\sigma^2N_2\sqrt{(\Omega_1{}^2 + \Omega_2{}^2)}$$

$$\Gamma_2 = \sqrt{2}\pi s_2{}^2N_2\Omega_2 + \pi\sigma^2N_1\sqrt{(\Omega_1{}^2 + \Omega_2{}^2)}.$$

These formulæ, which, like that obtained before, were first deduced by Maxwell,[1] allow of the simple interpretation that the number of collisions of both kinds of particles together is just as great as if the $N_1$ particles of the first kind were all moving with the speed $\Omega_1$ in one direction, and the $N_2$ particles of the second kind with the speed $\Omega_2$ in a perpendicular direction.[2]

These formulæ have been applied in § 97 and § 98 to the theory of diffusion, and have also been taken into account in § 104 in the investigation of heat-conductivity.

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[1] *Phil. Mag.* [4] xix. 1860, p. 27; *Scient. Papers*, 1890, i. p. 386.

[2] Stefan, *Wiener Sitzungsberichte*, lxv. Abth. 2, 1872, p. 349. [This interpretation does not apply to the first terms of the formulæ. To include these we may say that everything occurs as if the particles of the two kinds are all moving with the speeds $\Omega_1$ and $\Omega_2$ respectively, and that two colliding particles always meet at right angles.—Tr.]

## 31*. Number of Molecular Collisions in a Current of Gas

To be able to apply these formulæ to the theory of internal friction we have yet to determine the influence which a forward motion of a gas exerts on the collision-frequency of its molecules. If this motion at all points of the gas is characterised by the same speed and the same direction, the frequency of collisions can neither increase nor diminish. But a perceptible influence may result if layers move near each other with different velocities, as is shown by the experiments made to determine the viscosity. A state of things then arises by the mixing of layers, which we can represent with tolerable accuracy by supposing two masses of gas of the same kind and at the same temperature to be flowing in the same enclosure with unequal speeds.

Consider, therefore, two groups of gaseous molecules in the same vessel, which they fill with unequal densities; they further differ in the unequal speed of their flow, but are otherwise completely alike: Maxwell's law of distribution of speeds therefore holds in both groups in exactly equal fashion, provided that we apply it only to that part of the molecular motion which shows itself as heat, and therefore provided that from the motions of the individual molecules we subtract the progressive motion of the group as a whole. In the formulæ referring to the separate groups we have consequently to introduce the same value, not only for the molecular weight $m$, but also for the constant $k$, and this holds, too, for the radius of the sphere of action $s$. Suppose, further, that the flow has the same direction for both groups, and take this direction to be that of one of the axes of coordinates. Then the number of collisions per unit time of a particle of the first kind, of which there are $N_1$ per unit volume, is

$$\Gamma_1 = \pi s^2(\sqrt{2}\, N_1\Omega + N_2\gamma),$$

and that of a particle of the second kind, of which there are $N_2$ per unit volume, is

$$\Gamma_2 = \pi s^2(\sqrt{2}\, N_2\Omega + N_1\gamma),$$

wherein $\gamma$ is given by

$$\gamma = (km/\pi)^3\int_{-\infty}^{\infty} du_1\int_{-\infty}^{\infty} dv_1\int_{-\infty}^{\infty} dw_1\int_{-\infty}^{\infty} du_2\int_{-\infty}^{\infty} dv_2\int_{-\infty}^{\infty} dw_2\, r e^{-\phi}$$

$$r = \sqrt{\{(u_1-u_2)^2 + (v_1-v_2)^2 + (w_1-w_2)^2\}}$$

$$\phi = km\{(u_1-a_1)^2 + v_1{}^2 + w_1{}^2 + (u_2-a_2)^2 + v_2{}^2 + w_2{}^2\},$$

where $a_1$ and $a_2$ denote the speeds of flow of the two groups in the direction of $u$.

By substitution as before in the expression for $\gamma$ of

$$\begin{array}{ll} u_1 \equiv \mathfrak{U} + \tfrac{1}{2}\mathfrak{u} & u_2 \equiv \mathfrak{U} - \tfrac{1}{2}\mathfrak{u} \\ v_1 \equiv \mathfrak{V} + \tfrac{1}{2}\mathfrak{v} & v_2 \equiv \mathfrak{V} - \tfrac{1}{2}\mathfrak{v} \\ w_1 \equiv \mathfrak{W} + \tfrac{1}{2}\mathfrak{w} & w_2 \equiv \mathfrak{W} - \tfrac{1}{2}\mathfrak{w} \\ a_1 \equiv A + \tfrac{1}{2}a & a_2 \equiv A - \tfrac{1}{2}a, \end{array}$$

$\gamma$ assumes its former shape, while $r$ and $\phi$ become

$$r = \sqrt{(\mathfrak{u}^2 + \mathfrak{v}^2 + \mathfrak{w}^2)}$$

$$\phi = 2km\{(\mathfrak{U} - A)^2 + \mathfrak{V}^2 + \mathfrak{W}^2\} + \tfrac{1}{2}km\{(\mathfrak{u} - a)^2 + \mathfrak{v}^2 + \mathfrak{w}^2\}.$$

If we now introduce polar coordinates, the integrations with respect to $\mathfrak{U}$, $\mathfrak{V}$, $\mathfrak{W}$ are easily performed, and those with respect to $\mathfrak{u}$, $\mathfrak{v}$, $\mathfrak{w}$ partially so, the final shape of the integral being

$$\gamma = \frac{1}{a}\left(\frac{km}{2\pi}\right)^{\frac{1}{2}}\int_0^\infty d\psi\, \psi^2 \{e^{-\frac{1}{2}km(\psi - a)^2} - e^{-\frac{1}{2}km(\psi + a)^2}\},$$

which by development in powers of $a$ gives

$$\gamma = 2\sqrt{(2/\pi km)}\, e^{-\frac{1}{2}kma^2}(1 + \tfrac{2}{3}kma^2 + \ldots);$$

and this for $a = 0$ reduces to the known result

$$\gamma = \sqrt{2}\,\Omega.$$

If we also develop the exponential function in powers of $a$ we obtain

$$\gamma = 2\sqrt{(2/\pi km)}\,(1 + \tfrac{1}{6}kma^2 + \ldots),$$

which shows that the collision-frequency is increased by the flow of the gas by an amount which is of the order of the square of the difference $a \equiv a_1 - a_2$. This difference, or the relative velocity of two neighbouring layers, is in the theory of internal friction always looked upon as very small, and its square as therefore negligible. Here, too, it is a very small magnitude of the order of the molecular free path; and in the formula, which by introduction of the mean speed becomes

$$\gamma = \sqrt{2}\,\Omega\left\{1 + \frac{2}{3\pi}\left(\frac{a}{\Omega}\right)^2 + \ldots\right\},$$

we may neglect the correctional term as vanishingly small, and therefore apply to a flowing gas the same formulæ for the collision-frequency of its molecules as to a gas which possesses no other than its molecular heat-motion.

## 32*. Collision-frequency of a Particular Molecule

The collision-frequency of a molecule which moves with a given speed may be calculated, but not quite so easily as the mean collision-frequency of all the molecules. To calculate this number B we can, in the case of a single gas composed of exactly similar molecules, make use of the formula obtained in § 29*, viz.:—

$$\mathrm{B} = \pi \mathrm{s}^2 N (km/\pi)^{\frac{3}{2}} \int_{-\infty}^{\infty} dU \int_{-\infty}^{\infty} dV \int_{-\infty}^{\infty} dW \, r e^{-km(U^2+V^2+W^2)},$$

where

$$r = \sqrt{\{(U-u)^2 + (V-v)^2 + (W-w)^2\}}.$$

Since the velocity of the colliding molecule and its axial components are in general of finite magnitude we may put new variables $U+u$, $V+v$, $W+w$ for $U$, $V$, $W$ without altering the limits of the integrations; consequently

$$\mathrm{B} = \pi \mathrm{s}^2 N (km/\pi)^{\frac{3}{2}} \int_{-\infty}^{\infty} dU \int_{-\infty}^{\infty} dV \int_{-\infty}^{\infty} dW \sqrt{(U^2+V^2+W^2)} e^{-\chi},$$

where for shortness is put

$$\chi \equiv km\{(U+u)^2 + (V+v)^2 + (W+w)^2\}.$$

Since there is no distinction as regards direction, we may choose our coordinate system as we like, and, therefore, take the direction, in which the particle under consideration moves with the speed

$$\omega = \sqrt{(u^2+v^2+w^2)},$$

as that of one of the axes. If we further substitute polar coordinates $\psi$, $s$, $\phi$ in place of the Cartesian $U$, $V$, $W$ we have

$$\mathrm{B} = \pi \mathrm{s}^2 N (km/\pi)^{\frac{3}{2}} \int_0^{2\pi} d\phi \int_0^{\pi} ds \sin s \int_0^{\infty} d\psi \, \psi^3 e^{-q},$$

where

$$q \equiv km(\psi^2 + \omega^2 + 2\omega\psi \cos s).$$

On integration with respect to $s$ and $\phi$ this becomes

$$\mathrm{B} = \pi \mathrm{s}^2 \frac{N}{\omega} (km/\pi)^{\frac{1}{2}} \int_0^{\infty} d\psi \, \psi^2 \{e^{-km(\psi-\omega)^2} - e^{-km(\psi+\omega^2}\},$$

which can be put into another form

$$B = \tfrac{1}{2}\pi^{\frac{1}{2}}Ns^2\{\pi^{\frac{1}{2}}\Omega e^{-km\omega^2} + (4\omega + \tfrac{1}{2}\pi\Omega^2/\omega)\int_0^{\omega\sqrt{(km)}} d\mu\, e^{-\mu^2}\}.$$

I arrived at this last expression in 1866 in a Latin dissertation,[1] in which, starting with Clausius' formula, I deduced Maxwell's. From this value of B I calculated, by integration, the value of the mean collision-frequency

$$\Gamma = 4\pi^{-\frac{1}{2}}N(km)^{\frac{3}{2}}\int_0^{\infty} d\omega\ \omega^2 B e^{-km\omega^2},$$

and, by developing this in a series, obtained the same value

$$\Gamma = 2Ns^2\sqrt{(2\pi/km)} = \sqrt{2}\,\pi s^2 N\Omega,$$

which we have already found in a simple way.

The magnitude B denotes the number of collisions which a particle moving with speed $\omega$ experiences in unit time from an assemblage of $N$ other particles whose mean speed is $\Omega$. Closely allied to this expression is that of another magnitude

$$\pi s^2 N_2 \sqrt{(\Omega_1{}^2 + \Omega_2{}^2)},$$

which we deduced in § 30*; this represents the number of collisions that occur in unit time between a particle of a group whose mean speed is $\Omega_1$ and the $N_2$ particles of another group with mean speed $\Omega_2$. The chief difference between the two expressions is that $\omega$ denotes a speed of arbitrary amount, while $\Omega_1$ represents a mean value; but otherwise they are so similar that we might expect the formula

$$B = \pi s^2 N\sqrt{(\omega^2 + \Omega^2)},$$

which we have formed from that last given, to represent the number B with at least approximate accuracy.

This expectation is fairly well justified by the comparison of a few values of the exact ratio

$$\frac{B}{\Gamma} = \frac{1}{2\sqrt{2}}\left(e^{-km\omega^2} + \frac{4\omega^2 + \frac{1}{2}\pi\Omega^2}{\sqrt{\pi}\,\omega\Omega}\int_0^{\omega\sqrt{(km)}} d\mu\, e^{-\mu^2}\right)$$

with those of the approximate expression

$$\frac{B}{\Gamma} = \frac{\sqrt{(\omega^2 + \Omega^2)}}{\sqrt{2}\,\Omega} = \sqrt{(\tfrac{1}{2} + \tfrac{1}{8}\pi km\omega^2)}.$$

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[1] *Dissertatio de Gasorum Theoria*, Vratislaviæ 1866. Also in the first edition of this book, 1877, p. 294.

The following series of figures show that the two expressions agree remarkably well both for small and large values of $\omega$, while for middle values of $\omega$ a regular deviation occurs.

| $\omega/\Omega$ | $B/\Gamma$ | | Ratio |
|---|---|---|---|
| | Exact | Approximate | |
| 0 | ·707 | ·707 | 1 |
| 0·5 | ·781 | ·796 | 1·019 |
| 1 | ·975 | 1 | 1·026 |
| 2 | 1·553 | 1·581 | 1·018 |
| 3 | 2·214 | 2·236 | 1·010 |
| 4 | 2·898 | 2·916 | 1·006 |
| 5 | 3·591 | 3·606 | 1·004 |

The values obtained from the approximate formula are rather too large, but the errors are in all cases less than $2\frac{1}{2}$ per cent. The simple approximate formula can therefore very well be used instead of the more complicated exact formula in all calculations when absolute accuracy is not desired.

## 33*. Molecular Free Path

With each collision a molecule starts on a fresh rectilineal piece of its zigzag path. The number of collisions is therefore the same as that of the straight bits of the path traversed. Consequently we find the mean length of one of these bits by dividing the length of path traversed per unit time (which is measured by the velocity) by the number of collisions experienced per unit time.

Since mean values are taken in this calculation, our first thought is to divide the mean speed by the mean collision-frequency, and call the quotient the mean free path. In this way we have already obtained in § 28* the value

$$L' = \frac{G}{\mathrm{A}} = \frac{3}{4\pi s^2 N}$$

for the mean free path of the particles of a simple gas, from the assumption, which is approximately true, that the speeds of all the particles are the same. Instead of this value, which Clausius[1] gave, Maxwell[2] obtained the somewhat smaller value

$$L = \frac{\Omega}{\Gamma} = \frac{1}{\sqrt{2}\,\pi s^2 N},$$

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[1] *Phil. Mag.* 4, xix. p. 434, 1860; *Abhandl. ü. d. mech. Wärmetheorie*, Abth. 2, note to p. 265; *Mech. Wärmetheorie*, iii. p. 61, 1889–91.

[2] *Phil. Mag.* 4, xix. p. 28, 1860; *Scientific Papers*, Cambridge 1890, i. p. 387.

as follows at once from the formulæ of § 29*, by employing his law of distribution of speeds.

## 34*. Correction of the Formula by allowing for the Dimensions of the Molecules

The formula obtained for the free path may be further improved by a correction which van der Waals[1] first attempted to apply. The length as given by the formula is somewhat too great, since the calculation of the probability of collision in § 27* was conducted as if the space occupied by the sphere of action of a molecule between two collisions (or the fourfold volume of the path, as in § 69) were equal to a cylinder whose base is a central section of the sphere of action, and whose height is the free path —in a strict calculation we must remember that this space has hemispherical ends. Owing to this circumstance, the free path $L$ which the centre of a molecule traverses between two collisions is diminished by a magnitude of the order of $\varsigma$, the radius of the sphere of action.

In the case of central collisions the diameter of a molecule or the radius of its sphere of action would have to be subtracted, and a smaller amount in every other case. The mean value of the correction may be found by a simple integration over the hemisphere. The correction corresponding to an angle of impact $s$ made by the direction of the relative motion with that of the line of centres is $\varsigma \cos s$. The probability of this value of the angle of impact is obtained by projecting the ring-shaped element $2\pi \sin s\, ds$ of the spherical surface on the plane of the section and dividing by $\pi$, the area of this section; its value is $2 \cos s \sin s\, ds$, and consequently the mean value of the correction is

$$2\varsigma \int_0^{\frac{1}{2}\pi} \cos^2 s \sin s\, ds = \tfrac{2}{3}\varsigma.$$

Van der Waals, who instead of this had found the value $\frac{1}{2}\varsigma$, has given a more exact calculation in a later memoir.[2] He pointed out that the correction thus found does not refer to the absolute value of the molecular free path; it is rather the path of the colliding particle relatively to that encountered that has to be shortened by $\frac{2}{3}s$, and, of this shortening, part falls on the striking particle and part on that struck. If the former moves with a velocity whose components are $u$, $v$, $w$, and the latter with a velocity whose components are $U$, $V$, $W$, the path of the striking particle is diminished by

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[1] *Over de continuiteit van den gas- en vloeistoftoestand*, Leiden 1873, p. 48. Abstract in *Beiblätter*, 1877, i. p. 10. An English translation of F. Roth's version has been published by the Physical Society of London.

[2] *Arch. Néerl.* xii. p. 201, 1877.

$$\tfrac{2}{3}s\sqrt{\left\{\frac{u^2+v^2+w^2}{(u-U)^2+(v-V)^2+(w-W)^2}\right\}}$$

and that of the struck particle by

$$\tfrac{2}{3}s\sqrt{\left\{\frac{U^2+V^2+W^2}{(u-U)^2+(v-V)^2+(w-W)^2}\right\}}.$$

To find the average shortening of the paths of a particle with velocity components $u$, $v$, $w$ for all its collisions, we have to multiply the former number by the collision-frequency (§ 29*)

$$\pi s^2 N(km/\pi)^{\frac{3}{2}} dU\,dV\,dW\,r e^{-km(U^2+V^2+W^2)},$$

where

$$r \equiv \sqrt{\{(u-U)^2+(v-V)^2+(w-W)^2\}},$$

and integrate: the result is

$$\tfrac{2}{3}\pi s^3 N\sqrt{(u^2+v^2+w^2)}.$$

If now we multiply this expression by the probability of occurrence of the velocity $\omega \equiv \sqrt{(u^2+v^2+w^2)}$, viz.

$$4\pi^{-\frac{1}{2}}(km)^{\frac{3}{2}}\,\omega^2 d\omega\, e^{-km\omega^2}$$

(§ 18*), and integrate with respect to $\omega$ between the limits 0 and $\infty$, we obtain the value $\frac{2}{3}\pi s^3 N\Omega$, which we must divide by the mean collision-frequency $\Gamma \equiv \sqrt{2}\pi s^2 N\Omega$ in order to find the mean value of the correction

$$\frac{1}{3}\sqrt{2}\,s.$$

According to this calculation, on taking account of the magnitude of the molecules, we have to put for the value of the mean free path

$$L = \frac{1}{\sqrt{2}\pi s^2 N} - \frac{1}{3}\sqrt{2}\,s$$

$$= \frac{1}{\sqrt{2}\pi s^2 N}\left(1-\tfrac{2}{3}\pi s^3 N\right).$$

If instead of $N$, the number of molecules per unit volume, we introduce λ, the edge of the elementary cube containing one molecule as given by the relation

$$N\lambda^3 = 1,$$

we obtain

$$L = \frac{\lambda^3 - \frac{2}{3}\pi s^3}{\sqrt{2}\,\pi s^2}.$$

Advantageous use of this improved formula has been made in the investigation of the actual volume occupied by molecules (§ 117).

G. Jäger[1] has extended these considerations also to the theory of viscosity.

## 35*. Influence of Cohesion on the Free Path

W. Sutherland[2] has obtained a second correction of the formula which gives the molecular free path by calculating in what ratio the probability of collision between two particles is increased by their mutual attraction. We now proceed to give his calculation in order to put on a better footing what has been said in §§ 71 and 85 respecting this action of the forces of cohesion.

Since we need not calculate the absolute motion of both particles, but only their relative motion with respect to each other, we may take one to be fixed, while we ascribe to the other a velocity which is equal to the relative velocity with which they move relatively to each other. The path of the moving particle which is attracted by the fixed one lies in a plane which contains also the position of the fixed particle, and we may therefore denote the position of the moving particle at time $t$ with respect to the fixed particle at the origin by the coordinates $\rho$ and $\tau$ in that plane. The attraction, which depends on the radius $\rho$ only and is independent of the angle $\tau$, being denoted by $F(\rho)$, the motion is given by the differential equations

$$\ddot{\rho} - \rho\dot{\tau}^2 = -F(\rho)$$

$$\frac{1}{\rho}\frac{d}{dt}(\rho^2\dot{\tau}) = 0,$$

of which the second on integration leads to

$$\rho^2\dot{\tau} = h.$$

This constant $h$ represents twice the area of the surface described in unit time by the radius vector $\rho$, and we determine its value by consideration of a point on the orbit so distant from the origin that the attraction $F(\rho)$ may be taken as vanishingly small; the velocity is then constant, being that of the relative velocity $r$ with which the particles began to approach each other in straight paths, and the surface $h$ is then equal to the product $rb$, where $b$ is the length of the perpendicular from the fixed particle on the rectilineal part of the path of the moving particle.

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[1] *Wien. Sitzungsanz.* 1899, p. 89. [2] *Phil. Mag.* 1893 [5] xxxvi. p. 507.

The angular velocity is therefore

$$\dot{\tau} = br\rho^{-2},$$

and the first differential equation, on introduction of this value, becomes

$$\ddot{\rho} = b^2r^2\rho^{-3} - F(\rho),$$

which on integration gives

$$\tfrac{1}{2}\dot{\rho}^2 = C - \tfrac{1}{2}b^2r^2\rho^{-2} - \int d\rho F(\rho).$$

The constant $C$ may be determined by application of the equation at an infinitely great distance $\rho$ where the total velocity $r$ is given by the formula

$$r^2 = \dot{\rho}^2 + \rho^2\dot{\tau}^2,$$

while

$$\rho\dot{\tau} = h/\rho = 0$$

from a former equation. We thus finally obtain

$$\dot{\rho}^2 = r^2 - b^2r^2\rho^{-2} + 2\int_\rho^\infty d\rho F(\rho).$$

The shortest distance to which the particles approach each other is determined by the vanishing of $\dot{\rho}$, and thus by the equation

$$0 = r^2 - b^2r^2\rho^{-2} + 2\int_\rho^\infty d\rho F(\rho).$$

A collision ensues if this distance is less than the radius $\varsigma$ of the sphere of action, and this occurs if the perpendicular distance $b$ which satisfies the equation

$$b^2 = \rho^2\{1 + 2r^{-2}\int_\rho^\infty d\rho F(\rho)\}$$

is less than a limiting value, which we may put as

$$b^2 < \varsigma^2\{1 + 2r^{-2}\int_\varsigma^\infty d\rho F(\rho)\}\ ;$$

since for every value of $\rho$ which falls within the sphere of action, and is therefore less than $\varsigma$, we may assume that the function $F(\rho)$ is equal to 0, as this small distance is never reached.

If these gases had no cohesion, then $F(\rho)$ would be zero for every value of $\rho$, and the condition for the occurrence of a collision would be $b^2 < \varsigma^2$, as is obvious from the meaning of $b$, viz. the distance of the particle encountered from the path of the striking particle. The influence of the forces of cohesion on the frequency of the collisions and on the length of the free path therefore consists in the replacement in all calculations of the actual section $\pi\varsigma^2$ of the sphere of action by a larger area

$$\pi\varsigma^2\{1 + 2r^{-2}\int_\varsigma^\infty d\rho F(\rho)\}.$$

The magnitude by which the section has to be augmented depends on the temperature, and is, indeed, inversely proportional to the absolute temperature, as is shown by the occurrence in the denominator of the square of the molecular velocity $r$. This ratio was given in § 71, and its value was estimated in § 85 for the explanation of the observations on internal friction.[1]

In the next following investigations we shall for simplicity leave out of account both this correction and that given in § 34*.

## 36*. Free Path in Mixed Gases

In the case of a mixture of gases composed of molecules of two different kinds, we find the free path $L_1$ of a particle of the first kind and the free path $L_2$ of a particle of the second kind from the formulæ of § 30*, viz.

$$\{\sqrt{2}\pi\varsigma_1{}^2N_1\Omega_1 + \pi\sigma^2N_2\sqrt{(\Omega_1{}^2 + \Omega_2{}^2)}\}L_1 = \Omega_1$$
$$\{\sqrt{2}\pi\varsigma_2{}^2N_2\Omega_2 + \pi\sigma^2N_1\sqrt{(\Omega_1{}^2 + \Omega_2{}^2)}\}L_2 = \Omega_2;$$

taking account of the meaning of the magnitudes $\Omega$ we may write these

$$\{\sqrt{2}\pi\varsigma_1{}^2N_1 + \pi\sigma^2N_2\sqrt{(1 + k_1m_1/k_2m_2)}\}L_1 = 1$$
$$\{\sqrt{2}\pi\varsigma_2{}^2N_2 + \pi\sigma^2N_1\sqrt{(1 + k_2m_2/k_1m_1)}\}L_2 = 1,$$

and, in case the temperature of both components of the mixture is the same,

$$\{\sqrt{2}\pi\varsigma_1{}^2N_1 + \pi\sigma^2N_2\sqrt{(1 + m_1/m_2)}\}L_1 = 1$$
$$\{\sqrt{2}\pi\varsigma_2{}^2N_2 + \pi\sigma^2N_1\sqrt{(1 + m_2/m_1)}\}L_2 = 1.$$

These equations were first established by Maxwell.[2]

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[1] Compare the account of the observations on the friction of vapours in § 87.

*Phil. Mag.* [4] xix. p. 29, 1860; *Scientific Papers*, i. p. 388.

## 37*. Free Path of a Particle with a Given Speed

The values of the molecular free paths calculated in the preceding article are of the nature of average values, since they are deduced from the mean value of the speed $\Omega$ and from that of the collision-frequency $\Gamma$. We may therefore, for instance, look on the value

$$L = \Omega/\Gamma = 1/\sqrt{2}\pi s^2 N,$$

found for a simple gas, as a mean value of the paths which are traversed by the *whole* lot of particles moving with *different* speeds. But it is in no way to be considered as the probable or mean length of free path which any *one* single particle, moving with a *particular* speed, passes over without a collision.

To find the probability that any particle moving with speed $\omega$ traverses a path of length $x$ (or rather of a length between $x$ and $x + dx$) between successive collisions, we go back to the formulæ of § 26*, which give

$$e^{-x/l}\, dx/l$$

for this probability, $l$ being the mean length of the paths traversed by the molecules which move with the speed $\omega$. Since a particle with speed $\omega$ collides on an average B times in unit time with other particles, where B has the value given in § 32*, the path travelled in unit time is

$$\mathrm{B}l = \omega.$$

Thus the mean free path of the particle with speed $\omega$ is

$$l = \omega/\mathrm{B},$$

and the probability of a length $x$ being traversed with speed $\omega$ without disturbance, and for a collision to occur at its extremity, is

$$(\mathrm{B}/\omega)e^{-\mathrm{B}x/\omega}dx;$$

also the probability of the particle's traversing a path which exceeds the limit $x$ is

$$e^{-\mathrm{B}x/\omega}.$$

So as to show more clearly how the probability and mean free path $l$ depend on the speed $\omega$, in accordance with the above formulæ, I have calculated a few values of $\mathrm{B}/\Gamma$ and the corresponding values of $l/L \equiv (\Gamma/\mathrm{B})(\omega/\Omega)$ from the formula

$$\mathrm{B}/\Gamma = \frac{1}{2\sqrt{2}}\left\{ e^{-4\pi^{-1}(\omega/\Omega)^2} + \frac{4\omega^2 + \frac{1}{2}\pi\Omega^2}{\sqrt{\pi}\,\omega\Omega}\int_0^{2\pi^{-\frac{1}{2}}\omega/\Omega} d\mu\, e^{-\mu^2} \right\}.$$

and these I subjoin in the following table[1] :—

| $\omega/\Omega$ | $km\omega^2$ | $B/\Gamma$ | $l/L$ |
|---|---|---|---|
| 0 | | 0·70711 | 0 |
| 0·25 | | 0·72570 | 0·34450 |
| 0·5 | | 0·77988 | 0·64112 |
| 0·62666 | $\frac{1}{2}$ | 0·81946 | 0·76472 |
| 0·70711 | $\frac{1}{2}km\Omega^2$ | 0·84840 | 0·83345 |
| 0·88623 | 1 | 0·92219 | 0·96110 |
| 1 | $km\Omega^2$ | 0·97490 | 1·02575 |
| 1·25331 | 2 | 1·10523 | 1·13399 |
| 1·33333 | $\frac{16}{9}km\Omega^2$ | 1·14943 | 1·16000 |
| 1·41421 | $2km\Omega^2$ | 1·19531 | 1·18313 |
| 1·53499 | 3 | 1·26579 | 1·21267 |
| 1·66667 | $\frac{25}{9}km\Omega^2$ | 1·34490 | 1·23925 |
| 1·77245 | 4 | 1·40981 | 1·25723 |
| 2 | $4km\Omega^2$ | 1·55302 | 1·28781 |
| 2·25 | | 1·71440 | 1·31241 |
| 2·35 | | 1·77984 | 1·32034 |
| 2·5 | | 1·87884 | 1·33061 |
| 2·75 | | 2·04552 | 1·34440 |
| 3 | | 2·21388 | 1·35509 |
| 4 | | 2·89785 | 1·38034 |
| 5 | | 3·59107 | 1·39234 |
| 6 | | 4·28892 | 1·39895 |
| $\infty$ | | $\infty$ | 1·41421 |

The first, third, and fourth columns contain the ratios of the actual speed $\omega$ to the mean speed $\Omega$, of the probable collision-frequency $B$ to its mean value $\Gamma$, and of the probable free path $l$ to the mean free path $L$. The values of these ratios all increase together, as is shown by the curves on p. 430, which are plotted from the given numbers, the first representing the collision-frequencies, the second the free paths, as functions of the speed.

It is worth while to notice that the equalities $\omega = \Omega$, $B = \Gamma$, and $l = L$ do not occur simultaneously; but the mean collision-frequency is that of a particle which moves with a speed somewhat greater than the mean speed, and the mean free path is attained by a particle whose speed is rather less than the mean speed.

## 38*. Different Mean Values of the Free Path

In addition to the mean value of the molecular free path already calculated in § 33*, we can, by a slightly different calculation founded on these last considerations, deduce another mean value which is important for the development of our theory.

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[1] [Here $km\Omega^2 = 4/\pi = 1·27324$.—Tr.].

Of the $N$ molecules containéd in unit volume, Maxwell's law gives

$$4\pi^{-\frac{1}{2}}N(km)^{\frac{3}{2}}e^{-km\omega^2}\omega^2 d\omega$$

as the number which move with a speed $\omega$ or with a speed differing infinitely little from $\omega$. According to the preceding article these particles attain on the average a free path $l = \omega/\mathrm{B}$. If therefore $N$ is a number sufficiently great, the sum of all the paths which

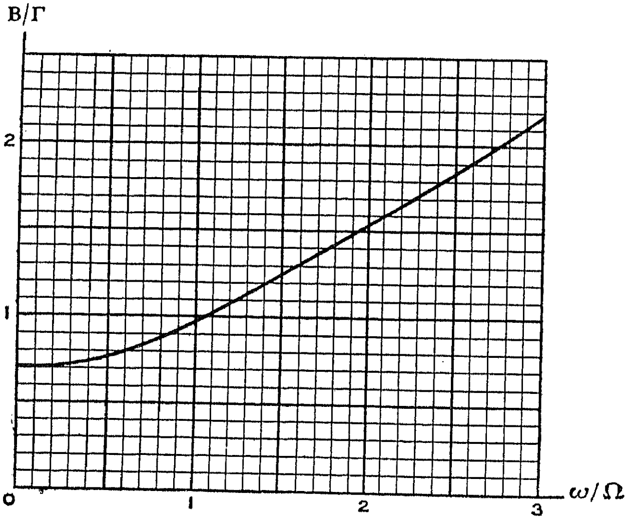

Fig. 5

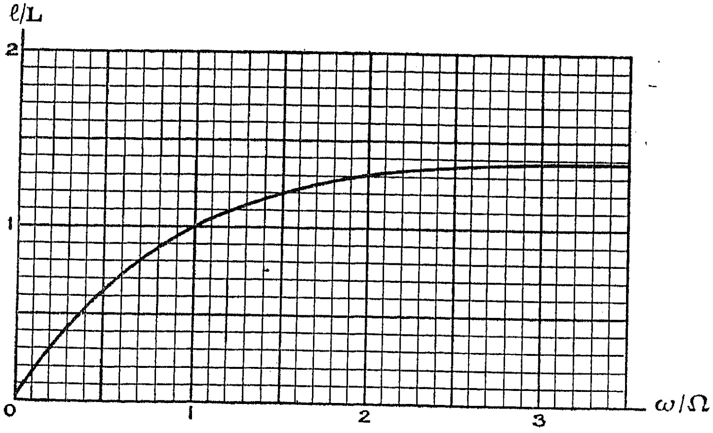

Fig. 6

are traversed between successive collisions by the particles in question is

$$4\pi\ {}^{\frac{1}{2}}N(km)^{\frac{3}{2}}le^{-km\omega^2}\omega^2d\omega = 4\pi^{-\frac{1}{2}}N(km)^{\frac{3}{2}}e^{-km\omega^2}(\omega^3/\mathrm{B})d\omega.$$

The sum, therefore, of all the paths which all the $N$ particles traverse in a straight line, *i.e.* between successive collisions, is given by the integral

$$4\pi^{-\frac{1}{2}}N(km)^{\frac{3}{2}}\int_0^\infty le^{-km\omega^2}\omega^2d\omega = 4\pi^{-\frac{1}{2}}N(km)^{\frac{3}{2}}\int_0^\infty d\omega(\omega^3/\mathrm{B})e^{-km\omega^2}.$$

From this total length of the paths of all the particles we obtain their average length, which we shall express by $M(l)$, by dividing by the number of particles $N$, viz.

$$M(l) = 4\pi^{-\frac{1}{2}}(km)^{\frac{3}{2}}\int_0^\infty d\omega\ \omega^2le^{-km\omega^2}$$

$$= 4\pi^{-\frac{1}{2}}(km)^{\frac{3}{2}}\int_0^\infty d\omega(\omega^3/\mathrm{B})e^{-km\omega^2}.$$

The mean value given by this formula is thus expressible as the arithmetic mean of all the values of the free path *l at any moment* for the whole number $N$ of the molecules contained in unit volume. We may thus take all the $N$ particles as starting at a given moment, each with its speed $\omega$, and then determine the mean value of the lengths of the paths attained at this *single* start.

We must distinguish this mean value from that which we obtain by considering the paths traversed by the particles *in the course of a prolonged time.* To find the mean in this other case we have to consider not only a single path traversed by any particle, but the whole of the B paths which it passes over backwards and forwards in the unit time. The sum of all the paths traversed in unit time is therefore given by the integral

$$4\pi^{-\frac{1}{2}}N(km)^{\frac{3}{2}}\int_0^\infty d\omega\ \omega^2\mathrm{B}le^{-km\omega^2} = 4\pi^{-\frac{1}{2}}N(km)^{\frac{3}{2}}\int_0^\infty d\omega\ \omega^3e^{-km\omega^2},$$

which is at once integrable, and leads to the value

$$2N/\sqrt{(\pi km)} = N\Omega.$$

But, according to § 32*, the number of these paths is

$$4\pi^{-\frac{1}{2}}N(km)^{\frac{3}{2}}\int_0^\infty d\omega\ \omega^2\mathrm{B}e^{-km\omega^2} = N\Gamma.$$

Consequently the mean value which we obtain from this other consideration is the value already obtained,

$$L = \Omega/\Gamma.$$

This mean value $L$ is greater than the other $M(l)$, since, in the summation of the B free paths $l$ of any particle, the larger values $l$ of the faster particles come more into account than when only one path for each particle is considered, as B too increases with the speed $\omega$.

We must give up the idea of calculating with exactness the mean value $M(l)$, by reason of the complicated form of the function B. But we can obtain an approximate value for $M(l)$ by a tolerably simple calculation if we substitute for B its approximate value

$$\mathrm{B} = \Gamma\sqrt{(\tfrac{1}{2} + \tfrac{\pi}{8}km\omega^2)}$$

as given in § 32*. If, then, we put

$$km\omega^2 \equiv \psi^2 - 4\pi^{-1},$$

the integral takes the form

$$M(l) = 4\sqrt{2}\,\pi^{-\frac{1}{2}}(\Omega/\Gamma)e^{4/\pi}\int_{2/\sqrt{\pi}}^{\infty} d\psi\,(\psi^2 - 4\pi^{-1})e^{-\psi^2},$$

which reduces to

$$M(l) = 4\sqrt{2}\,\pi^{-1}L\left\{1 - \left(\frac{4}{\pi} - \frac{1}{2}\right)\pi^{\frac{1}{2}}e^{4/\pi}\int_{2/\sqrt{\pi}}^{\infty} d\psi\,e^{-\psi^2}\right\};$$

and from this we may calculate the mean value. By the help of tables[1] of this integral we find

$$M(l) = 0{\cdot}937\,L.$$

This value is certainly less than $L$, but we must still remember that it is only approximate. For we have put too large a value for B, and have consequently got too small a value for $M(l)$. For the values of $\omega$, which occur the most frequently, the error in the approximation to B is about $2\frac{1}{2}$ per cent., and thus the factor 0·937 is too small by this amount. The mean value $M(l)$ is therefore about 4 per cent. smaller than $L$.

## 39*. Interval between Two Collisions

In calculating the average interval between two successive collisions of a particle with others, we can arrive at two different mean values, just as in the case of the free path. We might first consider all particles to start new paths at the same moment, and then ask how long the interval is, on the average, before one of the particles undergoes collision. Since a particle whose speed is $\omega$ collides on the average B times in unit time, the time that passes between successive collisions of this particle is on the average

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[1] Bessel, *Fundamenta Astronomiæ*, 1818, p. 36. Encke, *Astronomisches Jahrbuch für* 1834.

$$t = 1/\mathrm{B}.$$

Hence we should obtain the mean value for all the particles by multiplying this expression by Maxwell's expression for the probability of occurrence of the speed $\omega$, and by integrating from $\omega = 0$ to $\omega = \infty$.

The calculation is much simpler if we do not aim at finding the mean interval from any one collision to the next, but seek the average interval between two collisions that occur within a finite period, as, for instance, the unit of time. We then bring into reckoning, not the time of a single path of each molecule, but the time of all its paths; and to find the mean value divide, not by the number of particles, but by the number of paths. The mean value of the time between two successive collisions is then nothing else than the ratio of the whole interval to the mean number of the collisions that have occurred in this interval, viz.

$$T = 1/\Gamma = L/\Omega,$$

or the ratio of the mean free path to the mean speed.

This second mean value $T$ is less than that first named. For in its calculation the interval $1/\mathrm{B}$ is taken, not once, but B times for each particle, so that a smaller interval is taken oftener, and a larger interval more seldom.

## 40*. Calculation of the Pressure

Since the collision-frequency B is a transcendental function of the speed $\omega$, the theory frequently leads to formulæ that seem very complicated. But in a series of cases the calculation gives quite simple results.

As an instance, I proceed to calculate anew the pressure exerted by a gas, and this calculation can of course lead to no other result than that given by the general theory which was investigated in the first of these Mathematical Appendices.

We seek the pressure at an element of surface $df$, which we suppose is either in the interior of the space occupied by a gas or on the wall of the containing vessel. We take this surface-element at the origin of a system of rectangular coordinates $x$, $y$, $z$, whose directions we assume to be such that the direction of $x$ is perpendicular to $df$. Let an element of volume $dx\,dy\,dz$ be at a distance $r$ from $df$, and let the line $r$ make an angle $s$ with the negative direction of $x$. In the element $dx\,dy\,dz$ there are at each moment

$$4\pi^{-\frac{1}{2}}N(km)^{\frac{3}{2}}e^{-km\omega^2}\omega^2 d\omega\, dx\, dy\, dz$$

particles with speed $\omega$, of which each collides on an average B times per unit time with other particles and starts a new path. In unit time, therefore, there proceed from the element $dx\,dy\,dz$

$$4\pi^{-\frac{1}{2}}N(km)^{\frac{3}{2}}\mathrm{B}e^{-km\omega^2}\omega^2 d\omega\, dx\, dy\, dz$$

particles with speed $\omega$. Of these the number

$$N(km/\pi)^{\frac{3}{2}}\mathrm{B}e^{-km\omega^2}\omega^2 d\omega\, r^{-2}\cos s\, df\, dx\, dy\, dz$$

move in such a direction that the surface-element $df$ is met when the length of path is greater than, or at least equal to, the distance $r$. The number of the particles which traverse this distance without collision is

$$N(km/\pi)^{\frac{3}{2}}\mathrm{B}e^{-\beta r}e^{-km\omega^2}\omega^2 d\omega\, r^{-2}\cos s\, df\, dx\, dy\, dz$$

if $\beta$ is the reciprocal of the mean free path $l$, or

$$\beta \equiv 1/l = \mathrm{B}\omega.$$

To deduce from this number of the particles meeting $df$ the force exerted by them, we must multiply by

$$2m\omega\cos s,$$

if $df$ is part of the fixed wall, and integrate over the whole volume of the gas.

But if $df$ lies within the gas, we must multiply by $m\omega\cos s$ and integrate, and thus determine the momentum which passes through $df$ in unit time in the direction of increasing $x$, and subtract from this the momentum simultaneously carried over in the reverse direction.

The integrations are easily performed when the Cartesian coordinates $x$, $y$, $z$ are replaced by the polar coordinates $r$, $s$, $\phi$ given by

$$x = r\cos s,\quad y = r\sin s\cos\phi,\quad z = r\sin s\sin\phi.$$

We then have for the momentum carried over in unit time in the positive direction the expression

$$Q_1 df \equiv df Nm(km/\pi)^{\frac{3}{2}}\int_0^\infty d\omega\, \omega^3 e^{-km\omega^2}\mathrm{B}\int_0^\infty dr\, e^{-\beta r}\int_0^{\frac{1}{2}\pi} ds \sin s \cos^2 s\int_0^{2\pi} d\phi\,;$$

from this the momentum carried over in the negative direction, viz.

$$Q_2 df \equiv - df Nm(km/\pi)^{\frac{3}{2}}\int_0^\infty d\omega\, \omega^3 e^{-km\omega^2}\mathrm{B}\int_0^\infty dr\, e^{-\beta r}\int_{\frac{1}{2}\pi}^{\pi} ds \sin s \cos^2 s\int_0^{2\pi} d\phi,$$

differs only in sign and in two limits of integration. Therefore the pressure exerted (or the force per unit area) is given by the formula

$$p = 2Nm(km/\pi)^{\frac{3}{2}}\int_0^\infty d\omega\, \omega^3 e^{-km\omega^2}\mathrm{B}\int_0^\infty dr\, e^{-\beta r}\int_0^{\frac{1}{2}\pi} ds \sin s \cos^2 r\int_0^{2\pi} d\phi,$$

which is obtained more simply in the case when $df$ forms part of the wall of the containing vessel. On carrying out the integrations we obtain

$$p = N/2k,$$

for which may be written, in accordance with the formulæ of § 19*,

$$p = \tfrac{1}{3}NmG^2 = \tfrac{1}{8}\pi Nm\Omega^2.$$

A variation of this mode of carrying out the calculation, which deserves mention, consists in our introducing the time in which a path is traversed by a particle instead of the path itself. Among the particles contained in the element of volume $dx\,dy\,dz$ there are

$$4\pi^{-\frac{1}{2}}N(km)^{\frac{3}{2}}e^{-km\omega^2}\omega^2 d\omega\,\mathrm{B}e^{-\mathrm{B}t}dt\,dx\,dy\,dz$$

which continue for the interval $t$ without collision their straight path, which was begun with speed $\omega$, and then collide in the following element of time $dt$. Since the state of the gas does not alter with the time, there must come in just as many particles, which after the lapse of the time $t$ have acquired the velocity $\omega$, in the place of those which lose their former speed $\omega$. Therefore the number of particles which in unit time proceed from the element $dx\,dy\,dz$ with speed $\omega$, and collide after the lapse of time $t$, is

$$4\pi^{-\frac{1}{2}}N(km)^{\frac{3}{2}}e^{-km\omega^2}\omega^2 d\omega\; e^{-\mathrm{B}t}\mathrm{B}t^{-1}dt\,dx\,dy\,dz.$$

Of these the number

$$N(km/\pi)^{\frac{3}{2}}e^{-km\omega^2}\omega^2 d\omega\; e^{-\mathrm{B}t}\mathrm{B}t^{-1}dt\, r^{-2}\cos s\; df\,dx\,dy\,dz$$

reach the element $df$ if the time $t$ is sufficient for the length $r$ to be traversed, that is, if $\omega t > r$. From this we obtain the required pressure $p$ by multiplying by $2m\omega \cos s$, dividing by $df$, and integrating. If, again, we introduce polar coordinates, we have

$$p = 2Nm(km/\pi)^{\frac{3}{2}} \int_0^\infty e^{-km\omega^2} \omega^3 d\omega \int_0^\infty e^{-\mathrm{B}t} \mathrm{B} t^{-1} dt \int_0^{\omega t} dr \int_0^{\frac{1}{2}\pi} ds \sin s \cos^2 s \int_0^{2\pi} d\phi,$$

and this quintuple integration gives, as before,

$$p = N/2k = \tfrac{1}{3} NmG^2 = \tfrac{1}{8}\pi Nm\Omega^2.$$

## 41*. Number and Mean Collision-impulse of the Colliding Particles

The number of particles, by the collision of which against the walls of the vessel this pressure is set up, is easily calculated by the same methods. We obtain it from the foregoing formulæ by suppressing the factor $2m\omega \cos s$ in them. The result of the integration is that the unit area is struck by $\frac{1}{4}N\Omega$ particles in a unit of time; and since these give rise to the pressure $p = \frac{1}{8}\pi Nm\Omega^2$, the mean value of the impulse of a single particle is

$$\tfrac{1}{2}\pi m\Omega.$$

These considerations show that it is not right under all circumstances to calculate mean values in the mode invented (see § 10) by Joule and Krönig.

## 42*. Another Calculation of the Mean Free Path

Our formulæ may be employed with proportionate ease to calculate in another way the value of the mean free path.

The number of all the particles issuing in unit time from unit volume is

$$4\pi^{-\frac{1}{2}} N(km)^{\frac{3}{2}} \int_0^\infty \mathrm{B} e^{-km\omega^2} \omega^2 d\omega \int_0^\infty e^{-\beta r} \beta dr,$$

where $\mathrm{B}$ is again put for $\beta\omega$, and the sum of the paths traversed by them till they next collide is

$$4\pi^{-\frac{1}{2}} N(km)^{\frac{3}{2}} \int_0^\infty \mathrm{B} e^{-km\omega^2} \omega^2 d\omega \int_0^\infty e^{-\beta r} \beta r \, dr.$$

The values of these integrals respectively are

$$2\sqrt{(2\pi)} N^2 s^2/km \quad \text{and} \quad 2\sqrt{\pi}\, N/km,$$

and their ratio

$$L = 1/\sqrt{2}\, \pi N s^2$$

is the mean free path, as has already been found.

## 43*. Pressure of Air in Motion

The same calculations may also be made in the case when the mass of gas is in a state of flow, and we shall estimate the pressure exerted by a gas moving with constant velocity $a$ upon a surface in the mass of gas which we take at right angles to the direction of flow.

Since the forward velocity $a$ may be taken as equally shared by all the particles of the whole mass of gas, there is no need for this new problem to alter the formulæ of § 40* except by replacing the function $e^{-km\omega^2}$, expressive of Maxwell's law, by the more general function

$$e^{-km(\omega^2+a^2-2a\omega\cos s)}.$$

Two integrations then give

$$Q_1 = 2\pi Nm(km/\pi)^{\frac{3}{2}}\int_0^\infty d\omega\int_0^{\frac{1}{2}\pi} ds\, \omega^4 \sin s \cos^2 s\, e^{-km(\omega^2+a^2-2a\omega\cos s)}$$

for the momentum carried across unit area in unit time in the positive direction, and

$$Q_2 = -2\pi Nm(km/\pi)^{\frac{3}{2}}\int_0^\infty d\omega\int_{\frac{1}{2}\pi}^{\pi} ds\, \omega^4 \sin s \cos^2 s\, e^{-km(\omega^2+a^2-2a\omega\cos s)}$$

for that carried over in the negative direction; and the pressure exerted by the streaming gas in the direction of its flow is, according to the former formula, given by

$$p = Q_1 - Q_2.$$

Carrying out the integrations as far as we can, we obtain

$$Q_1 = Nm\surd(km/\pi)\left\{(a/2km)e^{-kma^2} + (a^2+1/2km)\int_{-a}^{\infty} d\omega e^{-km\omega^2}\right\},$$

or, on introduction of the mean value $\Omega$ (§ 19*),

$$Q_1 = \tfrac{1}{2}Nm\left[(\tfrac{1}{8}\pi\Omega^2 + a^2)\left\{1 + (4/\pi\Omega)\int_0^a d\omega e^{-km\omega^2}\right\} + \tfrac{1}{2}a\Omega e^{-kma^2}\right].$$

Similarly we have

$$Q_2 = -\tfrac{1}{2}Nm\left[(\tfrac{1}{8}\pi\Omega^2 + a^2)\left\{1 - (4/\pi\Omega)\int_0^a d\omega e^{-km\omega^2}\right\} - \tfrac{1}{2}a\Omega e^{-kma^2}\right];$$

and thus as result we get the simple formula

$$p = Nm(\tfrac{1}{8}\pi\Omega^2 + a^2),$$

which we also might have deduced, by a much simpler calculation, from the formula

$$p = 2\pi Nm(km/\pi)^{\frac{3}{2}}\int_0^\infty d\omega\, \omega^4 \int_0^\pi ds \sin s \cos^2 s\, e^{-km(\omega^2+a^2-2a\omega \cos s)}$$

or its equivalent

$$p = Nm(km/\pi)^{\frac{3}{2}}\int_{-\infty}^\infty du \int_{-\infty}^\infty dv \int_{-\infty}^\infty dw\, u^2 e^{-km\{(u-a)^2+v^2+w^2\}}.$$

We have obtained this formula in § 35 (p. 72) in the form

$$p = \rho(\tfrac{1}{3}G^2 + a^2),$$

and from it have drawn conclusions respecting the momentum and force of reaction of a stream of air, and also respecting the resistance of air.

The magnitude of the resistance is calculated in another way in some memoirs.[1] It has been thought that the formulæ for $Q_1$ and $Q_2$ may be interpreted as if $2Q_1$ represents the pressure which the forward face of a body moving with speed $a$ experiences in air, while $-2Q_2$ represents the pressure of the air against the hinder face. Then the difference of these two magnitudes

$$2(Q_1 + Q_2) = 2Nm\left\{ (4/\pi\Omega)(\tfrac{1}{8}\pi\Omega^2 + a^2)\int_0^a d\omega\, e^{-km\omega^2} + \tfrac{1}{2}a\Omega e^{-kma^2} \right\}$$

would give the resistance per unit area, and this reduces to

$$2(Q_1 + Q_2) = 2Nma\Omega(1 + 4a^2/3\pi\Omega^2)$$

on neglect of higher powers of $a$. The resistance would thus consist of two parts, of which one would be proportional to the first, and the other to the third, power of the speed $a$.

This mode of interpreting the formulæ was first employed by Hirn,[2] and the contradiction between his formula and experiment led him to raise objections to the validity of the kinetic theory, which were, however, answered by Clausius.[3] It is sufficient here to point out that the deduction of the expressions for $Q_1$ and $Q_2$ are not valid for a rigid bounding surface, but only for a hypothetical plane in the interior of the gas.

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[1] W. B. Smith, *Zur Molecular-Kinematik*, Göttingen 1879; E. Toepler, *Zur Ermittlung des Luftwiderstandes nach der kinetischen Theorie*, Wien 1886; G. Sussloff, *Journ. russ. phys.-chem. Ges.* xviii. p. 79, 1887.

[2] Hirn, 'Recherches sur la Résistance de l'Air en Fonction de la Température,' *Mém. de l'Acad. de Belgique*, xliii. (2) 1882.

[3] Clausius, 'Examen des Objections faites par M. Hirn,' *Bull. de l'Acad. de Belgique* [3] xi. p. 173, 1886.

# APPENDIX IV

## VISCOSITY OF GASES

### 44*. General Remarks on Viscosity

THE viscosity or internal friction of gases is, according to this theory, nothing else than the transference from one place to another of the momentum of translation or flow of the medium by means of the heat-motions of its particles. In order to find the magnitude of the force exerted by one layer upon another by reason of viscosity, we have to determine the amount of momentum which is carried over in unit time by the molecules as they move backwards and forwards across the separating plane or surface of friction.

Starting from this conception of the action, which has been explained more at length in § 73, I published, in a memoir [1] that appeared in 1865, a theory of viscosity which I will here first reproduce. However, since for easiness of calculation I then made the not strictly accurate assumption that all the molecules move with the same speed, I shall follow up this calculation, made in accordance with Clausius' assumption, by another which I shall found on Maxwell's law of the distribution of speeds.

### 45*. Theory of Viscosity on the Assumption of Equal Speeds for all Molecules

While I now ascribe at first to all molecules of the gas equal molecular or heat motions that occur equally in all directions, I assume, further, a forward movement of given magnitude and direction; of this I assume the direction to be the same at all points of the gas, but the magnitude to vary continuously from layer to layer. I consider, further, that this motion may be looked upon as vanishingly small in comparison with the heat-motions, though not actually small in itself; for, since the mean molecular speed which will be ascribed to all the molecules is very great, amounting to several hundred metres per second, the forward motion of even a tolerably quick flow, such as occurs with a speed of 10 metres per second, will seem of but little importance in comparison.

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[1] 'Ueber die innere Reibung der Gase,' erste Abhandlung. 'Ueber den Einfluss der Luft auf Pendelschwingungen,' *Pogg. Ann.* 1865, cxxv. p. 586.

Consider a system of rectangular coordinates $x$, $y$, $z$ such that the $y$-axis is parallel to the direction of the forward motion, and take the surface of friction, or the plane for which the friction between the gaseous layers on either side of it is to be determined, as perpendicular to the $x$-axis, and therefore parallel to the $yz$-plane, and let this plane pass through any arbitrary point in the medium with coordinates $x$, $y$, $z$. In this plane take an infinitely small rectangle with edges $dy$ and $dz$, and find the number of particles which pass through it and the amounts of momentum, which I will denote by $Q_1$ and $Q_2$, carried over it in both directions by these particles.

For this purpose consider an infinitely small volume-element $dx'dy'dz'$ at another point $(x', y', z')$ of the gas, and first determine the number of particles which, starting from it in a straight course, meet the surface $dy\,dz$ and pass through it. If $N$ is the number of molecules contained in unit volume, there are $N\,dx'dy'dz'$ particles in this volume-element at any moment; and if $T$ denotes the average interval between two successive collisions of a particle with others, the number of straight paths commenced in unit time by this group of molecules is

$$NT^{-1}dx'dy'dz';$$

this is also the number of particles which issue from the element in unit time in all directions.

Of these a portion, whose number is

$$NT^{-1}e^{-\beta r}dx'dy'dz',$$

traverse a path of length $r$ without a collision; herein $\beta L = 1$, or $\beta$ is the reciprocal of the mean free path $L$ which, on the assumption of equal speeds for all molecules, we have to put equal to the value found by Clausius[1], so that $\beta = \frac{4}{3}\pi s^2\lambda^{-3}$, $s$ and $\lambda$ denoting as before the radius of the sphere of action and the mean distance between neighbouring particles. Putting for $r$, which is still undetermined, the distance of the point $(x, y, z)$ from the point $(x', y', z')$, or

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[1] § 67 of the text, or § 33* of Appendix III.

$$r^2 = (x'-x)^2 + (y'-y)^2 + (z'-z)^2,$$

we may interpret the magnitude

$$NT^{-1}e^{-\beta r}dx'dy'dz'$$

as the number of particles which start from the element $dx'dy'dz'$ in unit time and traverse a sphere of radius $r$ described about the element as centre, so as to cut the surface-element $dy\,dz$. From the number of particles traversing the whole spherical surface we deduce the number of those crossing the element $dy\,dz$ by comparing the projection of the element on the spherical surface with the area of the whole sphere. The latter amounts to $4\pi r^2$, and the former to $dy\,dz \cos s$, where $s$ denotes the acute angle which the direction of $r$ makes with the $x$-axis. The number of particles, therefore, which in unit time reach and pass through the element $dy\,dz$, having started from the volume-element $dx'dy'dz'$, is

$$NT^{-1}e^{-\beta r}(4\pi r^2)^{-1} \cos s \; dy\,dz\,dx'dy'dz'.$$

The next question is, How much momentum is carried over by these particles? Since the molecular motion, of which heat consists, is taken to be the same throughout the medium, its transference causes no change, and it may therefore be left out of account, and we have to consider only the forward motion of the layers. Let this occur with velocity $v$ at the point $(x, y, z)$, and let $v'$ be the corresponding value of this function at the point $(x', y', z')$. Then the momentum leaving the element $dx'dy'dz'$ and crossing the element $dy\,dz$ in unit time is

$$dQ = (m/4\pi)NT^{-1}v'e^{-\beta r}r^{-2} \cos s \; dy\,dz\,dx'dy'dz'.$$

From this, by integration with respect to $x', y', z'$ over one-half of the medium, we obtain the total value of momentum carried over from this half of the medium through the element $dy\,dz$ of the dividing plane into the other half. If we take the medium as unlimited, this quantity which is carried over in the direction of increasing $x$ is

$$Q_1 = dy\,dz(m/4\pi)NT^{-1}\int_x^\infty dx'\int_{-\infty}^\infty dy'\int_{-\infty}^\infty dz'\, e^{-\beta r}v'r^{-2} \cos s,$$

while that carried over in the other direction is

$$Q_2 = dy\,dz(m/4\pi)NT^{-1}\int_{-\infty}^{x} dx'\int_{-\infty}^{\infty} dy'\int_{-\infty}^{\infty} dz'\,e^{-\beta r}v'r^{-2}\cos s.$$

The difference between these magnitudes

$$F \equiv Q_1 - Q_2,$$

or the sum of the gain and loss of one-half, is the friction exerted from the side of increasing $x$ upon the other; and so

$$-F \equiv Q_2 - Q_1$$

denotes the reaction exerted by the half corresponding to the smaller values of $x$ on the half with the larger values of $x$.

Since, as above assumed, $v$ is a continuous function of $x, y, z$, and therefore also $v'$ a continuous function of $x', y', z'$, Taylor's theorem gives the development

$$v' = v + (x'-x)\frac{dv}{dx} + (y'-y)\frac{dv}{dy} + (z'-z)\frac{dv}{dz} + \dots$$

After substitution of this series the integrations can be carried out, and present no difficulty if the rectilinear coordinates are replaced by polar coordinates whose origin is at the point $(x, y, z)$, *i.e.* by the coordinates $r$ and $s$ already introduced, and a second angle $\phi$ given by

$$\pm(x'-x) = r\cos s$$
$$\pm(y'-y) = r\sin s\cos\phi$$
$$\pm(z'-z) = r\sin s\sin\phi,$$

where the sign must be determined so that the acute angle $s$ may satisfy these relations. Then we obtain

$$Q_1 = dy\,dz(m/4\pi)NT^{-1}\int_0^{2\pi}\int_0^{\frac{1}{2}\pi}\int_0^{\infty} e^{-\beta r}v_1'\cos s\sin s\,dr\,ds\,d\phi$$

$$Q_2 = dy\,dz(m/4\pi)NT^{-1}\int_0^{2\pi}\int_0^{\frac{1}{2}\pi}\int_0^{\infty} e^{-\beta r}v_2'\cos s\sin s\,dr\,ds\,d\phi,$$

where for shortness we put

$$v_1' \equiv v + \frac{1}{1}\left(\frac{dv}{dx}\cos s + \frac{dv}{dy}\sin s\cos\phi + \frac{dv}{dz}\sin s\sin\phi\right)r + \dots$$

$$v_2' \equiv v - \frac{1}{1}\left(\frac{dv}{dx}\cos s + \frac{dv}{dy}\sin s\cos\phi + \frac{dv}{dz}\sin s\sin\phi\right)r + \dots$$

Remembering that $v$ and its differential coefficients are independent of the variables of integration, we get, on performing the integrations,

$$Q_1 = \tfrac{1}{2} dy\, dz\, mNT^{-1}\left(\frac{1}{2\beta}v + \frac{1}{3\beta^2}\frac{dv}{dx} + \frac{1}{4\beta^3}\frac{d^2v}{dx^2} + \dots\right)$$

$$Q_2 = \tfrac{1}{2} dy\, dz\, mNT^{-1}\left(\frac{1}{2\beta}v - \frac{1}{3\beta^2}\frac{dv}{dx} + \frac{1}{4\beta^3}\frac{d^2v}{dx^2} - \dots\right),$$

and thus by subtraction of these expressions the value of the friction exerted

$$F = dy\, dz\, mNT^{-1}\left(\frac{1}{3\beta^2}\frac{dv}{dx} + \frac{1}{5\beta^4}\frac{d^3v}{dx^3} + \dots\right).$$

The series obtained may be transformed into one proceeding by rising powers of the molecular free path, or, more correctly, of its square; for by substitution of the value $1/L$ for $\beta$ it becomes

$$F = dy\, dz\, mNT^{-1}\left(\frac{L^2}{3}\frac{dv}{dx} + \frac{L^4}{5}\frac{d^3v}{dx^2} + \dots\right);$$

and if the free path is really very small, this series will converge so rapidly that we may neglect all the terms after the first, and write for the friction

$$F = \tfrac{1}{3} mNT^{-1} L^2 (dv/dx) dy\, dz.$$

The friction is therefore proportional to the surface $dy\,dz$ on which it is exerted, and also to the differential coefficient of the forward velocity $v$ with respect to $x$, the direction of the normal to this surface. But this is Newton's hypothesis with respect to the nature of viscosity, according to which it is taken to be proportional to the relative velocity of the neighbouring layers, as has been explained more at length in § 74; for the relative velocity, or the difference of velocity, of two neighbouring layers is expressed by the value of the differential coefficient. Newton's hypothesis therefore gives the viscosity as expressible by

$$F = \eta \frac{dv}{dx} dy\, dz,$$

in which $\eta$ denotes the constant, which is called the *coefficient of viscosity*.

According to the theory just developed the value of this coefficient is

$$\eta = \tfrac{1}{3} mNT^{-1} L^2,$$

for which we may write (§ 75)

$$\eta = \tfrac{1}{3} m NGL \text{ or } \eta = \tfrac{1}{3}\rho GL,$$

where $\rho$ and $G$, as before, denote the density and mean speed of the molecules. If in this formula, which was first deduced by Maxwell,[1] we put the value of the mean free path given by Clausius' theory, we obtain

$$\eta = mG/4\pi s^2.$$

These expressions agree with those obtained in an elementary way in §§ 75 and 76.

## 46*. Calculation of Viscosity on the Assumption of Maxwell's Law of Distribution of Speeds

If we put on one side the inaccurate assumption that all the molecules have equal speeds, and replace it by Maxwell's law, as in our calculation of the pressure, we can at first introduce a simplification which is sufficient as an approximation. If the speed with which the gas flows is so small, as it is always assumed in the theory of viscosity, we can consider it as negligible in comparison with the very rapid motion of the molecules. It is then, therefore, allowable to employ Maxwell's law in the form which, strictly speaking, is valid only for the state of rest. In this manner Boltzmann[2] and Tait[3] have calculated the value of the coefficient of viscosity.

We arrive at the value of the momentum carried this way and that in unit time across the surface element $dy\,dz$ in the same manner as in the foregoing calculation. In unit volume there are

$$4\pi^{-\frac{1}{2}}N(km)^{\frac{3}{2}}e^{-km\omega^2}\omega^2 d\omega$$

particles with speed $\omega$, and therefore

$$4\pi^{-\frac{1}{2}}N(km)^{\frac{3}{2}}e^{-km\omega^2}\omega^2 d\omega\, r^2\, dr \sin s\, ds\, d\phi$$

in the volume-element $r^2 dr \sin s\, ds\, d\phi$; of these there pass over in the direction of $dy\,dz$, given by the angles $s$ and $\phi$, the number

$$dy\, dz N(km/\pi)^{\frac{3}{2}}e^{-km\omega^2}\omega^2 d\omega\, dr \cos s \sin s\, ds\, d\phi.$$

Each particle begins B new paths in unit time, where

$$\mathrm{B} \equiv \frac{\Gamma}{2\sqrt{2}}\left\{e^{-km\omega^2} + \frac{4\omega^2 + \frac{1}{2}\pi\Omega^2}{\sqrt{\pi}\,\omega\Omega}\int_0^{\omega\sqrt{(km)}} d\mu\, e^{-\mu^2}\right\};$$

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[1] *Phil. Mag.* [4] xix. p. 31, 1860; *Scientif. Works*, 1890, i. p. 390.

[2] *Wiener Akad. Sitzungsber.* 1881, lxxxiv. Abth. 2, p. 41.

[3] *Trans. R.S.E.* 1887, xxxiii. p. 259.

and the number of those which traverse the length $r$ without collision, and therefore pass through $dy\,dz$, is determined by the function

$$e^{-\mathrm{B}r/\omega}.$$

Thus the number of particles which in unit time pass through $dy\,dz$ with speed $\omega$ starting from a volume-element situated at the point $(x, y, z)$ is

$$dy\,dz N(km/\pi)^{\frac{3}{2}} e^{-km\omega^2} \mathrm{B} e^{-\mathrm{B}r/\omega} \omega^2 d\omega\, dr \cos s \sin s\, ds\, d\phi.$$

As before, we assume that each of these particles possesses the speed $v'$ with which the gas flows through the point given by $r, s, \phi$. Thus we obtain the value

$$Q = dy\,dz\, Nm(km/\pi)^{\frac{3}{2}} \int_0^\infty d\omega\, \omega^2 \mathrm{B} e^{-km\omega^2} \int_0^\infty dr\, e^{-\mathrm{B}r/\omega} \int_0^{\frac{1}{2}\pi} ds \sin s \cos s \int_0^{2\pi} d\phi\, v'$$

for the momentum which in unit time is carried over the element $dy\,dz$ in the one or the other direction, according as we put for $v'$ the values $v'_1$ or $v'_2$ given before; and the coefficient of friction is determined, as before, by double the value of the factor of $(dv/dx)dy\,dz$ in the development in series, or

$$\eta = 2Nm(km/\pi)^{\frac{3}{2}} \int_0^\infty d\omega\, \omega^2 \mathrm{B} e^{-km\omega^2} \int_0^\infty dr\, r e^{-\mathrm{B}r/\omega} \int_0^{\frac{1}{2}\pi} ds \sin s \cos^2 s \int_0^{2\pi} d\phi,$$

which reduces on integration to

$$\eta = \tfrac{4}{3} Nm(k^3m^3/\pi)^{\frac{1}{2}} \int_0^\infty d\omega\, e^{-km\omega^2} \omega^4/\mathrm{B},$$

or, as it may be written,

$$\eta = \frac{4m}{3\pi\varsigma^2\sqrt{(km)}} \int_0^\infty d\mu\, e^{-\mu^2} \mu^4 \left\{ e^{-\mu^2} + (2\mu + \mu^{-1}) \int_0^\mu d\mu\, e^{-\mu^2} \right\}^{-1}.$$

The value of this integral has been calculated by Boltzmann and also by Tait. The former found

$$\eta = 0{\cdot}088942636\, m/\varsigma^2\sqrt{(km)},$$

and with this Tait's[1] value agrees, as well as one calculated by Conrau,[2] of which I have been privately informed. Using the mean values of the speed and free path, viz.

$$\Omega = 2/\sqrt{(\pi km)}, \quad L = 1/\sqrt{2}\pi\varsigma^2 N,$$

we find finally

$$\eta = 0{\cdot}350203\, \rho\Omega L = 0{\cdot}322648\, \rho G L.$$

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[1] Compare Boltzmann, *Wiener Sitzungsber.* 1887, xcvi. Abth. 2, p. 895.

[2] See § 48*.

The numerical factor, which is the same for all gases, does not materially differ from that which has been calculated on the assumption of equality of speed for all molecules.

## 47*. Calculation from Maxwell's General Law

Even this improved calculation cannot lay claim to perfect accuracy. Instead of the law of distribution which is valid for the state of rest, must be employed the law that holds for a gas in a state of flow.

Maxwell's law can of course be extended without difficulty to the case wherein the mass of gas has a forward motion, as has been shown in §§ 16* and 18*. But this generalisation has reference only to the particular case wherein the forward motion has the same direction and speed at all points in the whole mass of gas. Those formulæ, therefore, are not directly applicable to our case, in which the gas is divided into layers which slide past each other with unequally quick motion.

The formulæ can, however, be taken with sufficient approximation as applicable, if their use is limited to so small a region that within it the forward motion of the gas may be considered as everywhere the same in magnitude and direction. Now the transference of momentum, in which, according to the kinetic theory, the process of internal friction consists, is carried on by a molecule no further than the molecule itself moves: it depends, then, on processes in such limited spaces that their dimensions may be compared with the mean length of the molecular free paths. And within such spaces we may look on the speed of the flow as uniform.

This assumption may be justified quite independently of the hypotheses of the kinetic theory, and simply by means of the assumptions upon which Newton based the theory of viscosity. The validity of the formulæ of this theory depends on the limitation that the velocities of the flow in separate layers which slide past each other are taken to be only very slightly different; the difference in the motion of neighbouring layers is to be taken as so small that, in comparison with the first power of the difference of the velocities, all higher powers may be neglected as vanishingly small.

On these grounds we here employ the formulæ of §§ 16* and

18* without hesitation, taking the forward motion to be uniform within each layer, but to differ from one layer to another.

In the formulæ which we introduce with this assumption we must partly alter the meaning of the symbols, in order to be able to retain the notation employed in the last two paragraphs and the system of rectangular coordinates there introduced. We had before denoted by $s$ the angle which the direction of motion of the particle under consideration makes with the direction of the forward velocity $o$ of the flowing gas; instead of $\cos s$ we have now to put $\sin s \cos \phi$, if, as hitherto, we take the direction of flow coincident with that of the $y$-axis. Corresponding to this assumption we replace the letter $o$ by $v'$, to which we leave the meaning it has hitherto had. The formulæ of the preceding paragraphs are thereby changed so far that the exponent $km\omega^2$, which occurs in Maxwell's formula, is to be replaced by

$$q \equiv km(\omega^2 + v'^2 - 2\omega v' \sin s \cos \phi).$$

The number $B$ of collisions which a single particle undergoes on the average in unit time, and the number of paths which it begins in unit time, are calculated just as if the gas were at rest. For, firstly, with our assumption the speed of flow alters by only vanishingly small quantities with the region in which the paths of the molecules considered lie; and, secondly, the calculation of § 31* teaches that with an unequal distribution of the forward motion the number of collisions is altered only by quantities of the order of the square of the differences of the speeds.

We put therefore

$$dy\, dzN(km/\pi)^{\frac{3}{2}}e^{-q}\mathrm{B}e^{-\mathrm{B}r/\omega}\omega^2\, d\omega\, dr \cos s \sin s\, ds\, d\phi$$

for the number of particles which pass through the surface-element $dy\, dz$ in unit time, having started from the volume-element $r^2 dr \sin s\, ds\, d\phi$, B retaining its former meaning.

Each of these particles possesses the momentum $m\omega \sin s \cos \phi$ in the direction of the $y$-axis; hence the momentum which is carried across the element $dy\, dz$ in unit time is

$$Q = dy\, dz\, mN(km/\pi)^{\frac{3}{2}} \int_0^\infty dw \int_0^\infty dr \int_0^{\frac{1}{2}\pi} ds \int_0^{2\pi} d\phi\, \mathrm{B}e^{-\mathrm{B}r/\omega} e^{-q}\, \omega^3 \sin^2 s \cos s \cos \phi;$$

and this expression gives the momentum $Q_1$, which is carried across in the direction of decreasing $x$, if the value $v'_1$, as defined in § 45*, is substituted for $v'$ in $q$, and also the momentum $Q_2$, which is carried over in the opposite direction, when $v'_2$ is put for $v'$.

In this formula the function B, which expresses the probability of a collision, is, strictly speaking, not only dependent on the velocity $\omega$, but also varies with place, that is with $r$, since the gas is not in the same state of motion at all points. We may, however, neglect this variation, and take B to have the same value everywhere if we retain the assumption that the velocities $v$ and $v'$ of the forward motion may be looked upon as vanishingly small in comparison with the mean speed $\Omega$ of the heat-motion.

In this approximation we can further neglect the square of $v'$ in comparison with $\omega^2$, and put

$$e^{-q} = e^{-km\omega^2}(1 + 2km\omega v' \sin s \cos \phi),$$

by which the integrations become partly practicable, and we obtain a development in a series proceeding by powers of $\omega/\mathrm{B} \equiv l$, which we may limit to its first terms ; we then have

$$Q_1 = (\gamma v + \tfrac{1}{2}\eta\ dv/dx)dy\,dz,$$

and also

$$Q_2 = (\gamma v - \tfrac{1}{2}\eta\ dv/dx)dy\,dz,$$

wherein

$$\gamma = \tfrac{1}{4}mN\Omega$$

$$\eta = \frac{2^8}{15\pi^3}\,\frac{mN}{\Omega^5}\int_0^\infty d\omega\,\omega^5 l e^{-km\omega^2}.$$

The last formula gives the value of the coefficient of friction of the gas.

## 48*. Investigation and Development of the Formula for the Coefficient of Viscosity

This formula is as little integrable as Boltzmann's; but even thus it is not difficult to grasp its meaning and deduce from it the laws of internal friction, just as from the formulæ first obtained.

We first of all easily see that by this calculation too the value of the coefficient of viscosity is *proportional to the square root of the absolute temperature.* For if in the formula for $\eta$, which may be written

$$\eta = \tfrac{8}{15}\pi^{-\frac{1}{2}}Nm(km)^{\frac{5}{2}}\int_0^\infty d\omega\, e^{-km\omega^2}\omega^6/\mathrm{B},$$

we put the value of B given in § 32*, viz.

$$B=Ns^2\sqrt{(\pi/km)}\left[e^{-km\omega^2}+\{(2km\omega^2+1)/\omega\sqrt{(km)}\}\int_0^{\omega\sqrt{(km)}}d\mu\, e^{-\mu^2}\right],$$

and substitute for $km\omega^2$ a new variable, the constant $k$ under the sign of integration disappears, and $\eta$ becomes inversely proportional to $\sqrt{(km)}$, *i.e.* directly proportional to the mean molecular speed $\Omega$, and therefore directly proportional to the square root of the absolute temperature.

If, lastly, in the final formula of the foregoing paragraph we replace the free path $l$ of the particles which move with the speed $\omega$ by the mean free path $L$ given by the equation

$$l/L=\omega\Gamma/\Omega B=(\omega/\Omega)f(km\omega^2),$$

which results from those obtained in § 37*, we see that $\eta$ is also proportional to $L$, and may be expressed by a formula of the form

$$\eta=\kappa mN\Omega L,$$

in which $\kappa$ is a numeric which is independent of $m$ and is thus *the same for all kinds of gases.*

The equation now appears in the same shape as before in the approximate calculation, and therefore directly shows that the law is still valid which lays down that *the viscosity of a gas is independent of its density.*

The value of the factor $\kappa$ is given by an integral which, though not integrable, is easily interpretable. If, in agreement with a notation already used in another calculation, we express the mean value of a function of the speed, as calculated on Maxwell's law of probability, by

$$M\{F(\omega)\}\equiv 4\pi^{-\frac{1}{2}}(km)^{\frac{3}{2}}\int_0^\infty d\omega\,\omega^2F(\omega)e^{-km\omega^2}$$

$$\equiv 2^5\pi^{-2}\Omega^{-3}\int_0^\infty d\omega\,\omega^2F(\omega)e^{-km\omega^2},$$

then

$$\eta=\tfrac{8}{15}\pi^{-1}Nm\Omega^{-2}M(\omega^3l).$$

By means of this interpretation of the integral as a mean value we are enabled to assign limits within which the value of the numeric $\kappa$ must lie.

The mean value in the formula is to be formed exactly as the mean value $M(l)$, which is introduced in § 38* with the like notation. The arithmetical mean, therefore, of all values of the product

$\omega^3 l$ for the whole of the $N$ molecules in unit volume is to be found, wherein $l$ denotes the length of a path already begun, and $\omega$ the speed with which it is traversed. Thus for each particle we are concerned only with the *single* path which has been begun.

In § 38* we also formed another mean value by considering for each particle all its paths traversed during a lengthened period. If we also now take into account all the paths traversed in unit time, we have to bring into the calculation B paths instead of a single path. This process results in a larger mean value, since the number B and the free path $l$ are (by § 37*) the larger the larger the speed $\omega$. This second mean value is defined by the formula

$$\mathfrak{M}(\omega^3 l) \equiv 4\pi^{-\frac{1}{2}}\Gamma^{-1}(km)^{\frac{3}{2}}\int_0^\infty d\omega\,\omega^5 l \mathrm{B} e^{-km\omega^2}$$

$$\equiv 4\pi^{-\frac{1}{2}}\Gamma^{-1}(km)^{\frac{3}{2}}\int_0^\infty d\omega\,\omega^6 e^{-km\omega^2},$$

which shows that our new consideration is simply equivalent to replacing the collision-frequency B by its mean value $\Gamma$. The formula leads to the value

$$\mathfrak{M}(\omega^3 l) = 15/4\Gamma k^2 m^2 = \tfrac{15}{64}\pi^2\Omega^2 L.$$

If we put this in the formula for the coefficient of viscosity, we obtain the equation

$$\eta = \tfrac{1}{8}\pi m N \Omega L,$$

first given by Stefan,[1] which gives too great a value.

On the other hand, we get too small a value for the coefficient if we substitute for the variable free path $l$ its mean value $L$, that is a length which is too great for small values of $\omega$, and too small for large values of $\omega$, so that in the calculation of the mean the smaller values come more into account than the larger. We have therefore

$$\eta > \frac{2^8 m N L}{15\pi^3\Omega^5}\int_0^\infty d\omega\,\omega^5 e^{-km\omega^2},$$

or

$$\eta > \tfrac{4}{15} m N \Omega L.$$

For the value of the coefficient $\kappa$, therefore, we obtain the following limits:—

$$\frac{4}{15} < \kappa < \frac{\pi}{8},$$

or

$$0{\cdot}27 < \kappa < 0{\cdot}39,$$

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[1] *Wiener Sitzungsber.* 1872, lxv. Abth. 2, p. 363.

which may be drawn somewhat closer. For, from the remark that the least value of B is $\Gamma/\sqrt{2}$, it follows, for instance, that

$$\kappa < 0{\cdot}37.$$

Accurate knowledge of this coefficient can only be obtained from a numerical evaluation of the integral by which the viscosity-coefficient is expressed. I have, therefore, already calculated the value of the integral for the first edition of this book, and I then obtained the value $\kappa = 0{\cdot}318$. But, since in this calculation I used only ten of the values of the free path given in § 37*, and also employed only the simplest process of mechanical quadrature, the value obtained could only be approximately accurate.

A more exact calculation was made in 1892 at the instance of E. Dorn, of Halle, by one of his pupils, Wilhelm Conrau, of Magdeburg, now deceased, with the help of tables which were even more complete than those published by Tait[1], and by the use of Cotes's formulæ. This calculation has given the somewhat smaller value

$$\kappa = 0{\cdot}30967,$$

which is said to be correct to all five places of decimals. I have tested this calculation in different ways, firstly by repeating my former calculation with a greater number of calculated values of $l$, by which I found the value $\kappa = 0{\cdot}311$, and, secondly, by a different process of calculation, viz. by breaking up the integral, which stretches from 0 to $\infty$, into a number of parts, and putting $l$ in each part equal to a linear function of $\omega$, whereby the integrations can be performed; this process, which by reason of the curvature of the curve that represents $l$ as a function of $\omega$ can only give too small values, gave $\kappa = 0{\cdot}308$. The number found by Conrau lies half-way between these two approximate values, and may, therefore, be assumed to be accurately calculated. Besides, P. Neugebauer, who has had the goodness to carry out similar calculations for the theory of the conduction of heat in gases which is given in § 57*, has tested Conrau's numbers, so far as was necessary for his purpose, by forming the first, second, third, and fourth differences, and has thereby found only unimportant errors which can be of no influence on the figures given.

I therefore consider

$$\eta = 0{\cdot}30967\, mN\Omega L$$

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[1] *Trans. R.S.E.* 1887, xxxiii. p. 277.

as the correct formula for the coefficient of viscosity, and I have employed it in Chap. VII. in all the calculations of the numerical values of the molecular free paths $L$.

Even this calculation of the factor $\kappa$ depends, indeed, on assumptions which are not exact, but only approximate. As has already been mentioned in § 47*, objection can especially be raised that the law of distribution of speeds has been employed in a form which is exact only for a constant flow, and that the collision-frequency and the mean free path have been so taken as if the gas were at rest. I cannot, therefore, gainsay Boltzmann's[1] expectation that another value of $\kappa$ would result from stricter regard being paid to these considerations. But hitherto no one has succeeded in overcoming the mathematical difficulties of a more accurate calculation, and in bringing out from it a final formula so simple that it can be turned to use for application to observed magnitudes; and, even if this were done, the result would not practically differ from that given by the above formula, which certainly does not depart much from the truth.

## 49*. Friction Accompanying Change of Density

In addition to the kind of internal friction that has been considered in the foregoing investigations, and which takes place in like fashion in both liquids and elastic fluids, there can be exhibited in the latter class of fluids a second kind of friction which has hitherto not been experimentally investigated. The motion does not undergo frictionlike resistance only when one layer slides over or near another; but such motions also as lead to compression or expansion are hindered by resistances, and these too we may term internal friction, since they spring from the same causes. These kinds of frictional forces which occur on compression or expansion have, therefore, been considered in all theories hitherto put forward of the viscosity of gases; and it has not escaped notice that this second kind of frictional forces may depend on a different coefficient of viscosity. For as the elasticities of extension and tension require two different values of the constant of elasticity, so also the friction that comes into play with dilatation may be determined by quite a different coefficient of friction from that concerned in the frictional phenomena hitherto exclusively considered, in which the molecules slide or roll over each other without, on the average, coming nearer to or going further from each other. But the different mathematical theories do not agree together in respect to the numerical ratio of these two coefficients of friction.

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[1] 'Theorie der Gasreibung,' *Wiener Sitzungsber.* Abth. 2, 1880, lxxxi. p. 117; 1881, lxxxiv. pp. 8, 1230.

The value which the kinetic theory of gases requires for the second coefficient of friction can be calculated from the same formulæ as before, if only the single alteration is made, that instead of the velocity-component $v$, which is parallel to the surface of friction $dy\,dz$, we consider a velocity $u$ perpendicular to it. We have, consequently, in the formula given in § 47* for the momentum carried across the element $dy\,dz$, no further change to make than to employ the exponent $q$ with the value

$$q \equiv km(\omega^2 + u'^2 - 2\omega u' \cos s)$$

and to exchange the factor $m \sin s \cos\phi$ for $m \cos s$. Thus the momentum normal to the surface of friction which is carried over $dy\,dz$ in unit time is

$$Q = dy\,dz\,mN(km/\pi)^{\frac{3}{2}} \int_0^\infty d\omega \int_0^\infty dr \int_0^{\frac{1}{2}\pi} ds \int_0^{2\pi} d\phi\, Be^{-Br/\omega} e^{-q} \omega^3 \sin s \cos^2 s\,;$$

on carrying out the integrations with the assumption that

$$u' = u \pm \frac{1}{1}\left(\frac{du}{dx}\cos s + \frac{du}{dy}\sin s \cos\phi + \frac{du}{dz}\sin s \sin\phi\right)r + \ldots$$

which corresponds to a former assumption, and that

$$e^{-q} = e^{-km\omega^2}(1 + 2km\omega u' \cos s)$$

with sufficient approximation, we find the values

$$Q_1 = -\tfrac{1}{2}p + \gamma' u + \tfrac{1}{2}\eta'\, du/dx$$

$$Q_2 = \tfrac{1}{2}p + \gamma' u - \tfrac{1}{2}\eta'\, du/dx,$$

where

$$p \equiv \tfrac{1}{8}\pi m N \Omega^2$$

is the pressure, and $\gamma'$ and $\eta'$ are constants whose meaning is

$$\gamma' = \tfrac{1}{2} m N \Omega = 2\gamma$$

$$\eta' = \frac{2^8 mN}{5\pi^3\Omega^5}\int_0^\infty d\omega\, \omega^5 l e^{-km\omega^2} = 3\eta.$$

The latter is the second coefficient of viscosity for which we are seeking; $\gamma'$ disappears from the difference $Q_2 - Q_1$ between the momenta carried the one way and the other, which has the value

$$Q_2 - Q_1 = p - \eta'\, du/dx = p - 3\eta\, du/dx.$$

Our theory agrees, therefore, with all the older theories in giving the value of the friction that accompanies alterations of density as larger than that of the ordinary friction. The ratio we have found of 3 : 1 is the same as that which, on Poisson's theory, should hold between the elastic constants of extension and torsion. In a theory of friction which I formerly developed from other hypotheses[1] I found the same value for this ratio. Its determination has, however, but slight practical value, since, as indeed the last formula shows, this kind of friction gives rise to forces which are not distinguished from the pressure, and may therefore be reckoned in the value of the pressure.

## 50*. External Friction

The considerations and formulæ of § 47* at once supply the means of determining the external friction which a gas experiences at the surface of a solid body.

Consider a gas which flows along the surface of a body at rest and has everywhere the same velocity $v$; then in each unit of time a number of particles, which have the momentum

$$Q = \gamma v = \tfrac{1}{4} m N \Omega v$$

in the direction of flow, strike unit of surface and rebound from it. Each particle rebounds from the solid wall with the same speed with which it struck it, but not always in a direction inclined to the wall at the same angle as that of the impact; for the solid wall, which is made up of molecules grouped together, is, in respect of a striking molecule, an exceedingly rough surface. Therefore the colliding molecules lose a part of their momentum in the direction parallel to the wall, and this becomes transformed into heat-motion. This loss appears as external friction, whose intensity, therefore, is given by the expression

$$\beta Q = \tfrac{1}{4} \beta m N \Omega v,$$

where $\beta$ is a numerical coefficient.

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[1] *Crelle's Journal für Mathematik*, 1873, lxxviii. p. 130; with Addition lxxx. p. 315, with improvements by Stefan and Boltzmann. Other theories of internal friction have been given by Navier (*Mém. de l'Acad. de Paris*, 1823, vi. p. 389), Poisson (*Journ. de l'Éc. Poly.* 1831, xiii. cah. 20, p. 139), Stokes (*Camb. Phil. Trans.* 1849, viii. p. 287), Cauchy (*Exerc. de Math.* 1828, 3rd year, p. 183), Barré de St. Venant (*Comptes Rendus*, 1843, xvii. p. 1240), and Stefan (*Wiener Sitzungsber.* 1862, xlvi. Abth. 2, p. 8).

This factor $\beta$ need not be a pure fraction. If the wall is very rough, many of the particles meeting it will be jerked back by its unevennesses with an oppositely directed motion; they undergo, then, a diminution of their velocity $v$ by an amount which may rise to $2v$. It may consequently be very possible that the particles which strike upon the wall receive a mean motion which is oppositely directed to their initial motion, as certainly in like manner occurs at the edge of flowing water; and in this case we should have to assume $\beta > 1$. According to Kundt and Warburg's observations, which were discussed in § 83, it appears that

$$\beta = \tfrac{5}{4},$$

whence the coefficient of external friction would have to be put

$$\varepsilon = \beta\gamma = \tfrac{5}{16} mN\Omega.$$

The assumption herein contained, that the striking molecules lose their whole velocity of translation and gain an opposite one, is not in contradiction with the fact that the gases slide along solid surfaces with a sensible speed; for not all the molecules of the surface layers of gas lose their velocity, but only those that strike against the solid surface.

# APPENDIX V

## *DIFFUSION*

### 51*. General Theory of Diffusion

IT is not my intention to investigate the theory of diffusion of gases with the same mathematical rigour as the simpler theory of viscosity. I limit myself here to supplying the mathematical explanations desirable for those going more deeply into the theory of diffusion developed in the text, and these I shall found upon Maxwell's law.

As to the distribution of the two gases, I make only the assumption that the whole pressure of the mixture

$$p = p_1 + p_2 = P$$

possesses everywhere the same constant value $P$, and therefore keeps this same value always; and also that, corresponding to it, there are always at every point the same number

$$N_1 + N_2$$

of molecules of the two kinds in unit volume.

As in the investigation given in the text, we determine for one of the two kinds of gas the number of molecules which in unit time pass in the direction of increasing $x$ through a surface-element $dS$ of a section of the diffusion tube at a distance $x$ from the beginning of the tube. We form this sum with the assumption of the validity of Maxwell's law of distribution of speeds. This assumption is not strictly admissible, since the deduction of this law presupposes the state of motion of the whole gas to be everywhere the same. But the application of this law to our problem is allowable as a good approximation, if we can look upon the ratio of mixture of the two gases in the space filled by them, not simply as a continuous function of the position, but also as one that varies very slowly. For, with this hypothesis, that ratio and the whole state of the mixture can be assumed to be constant within a tolerably large region, throughout which, therefore, Maxwell's law may be considered to hold.

According to a formula which we have developed before, and used several times, the element $dS$ is reached by a number

$$N(km/\pi)^{\frac{3}{2}}\mathrm{B}e^{-\mathrm{B}r/\omega}e^{-km\omega^2}\omega^2\,d\omega\;dS\cos s\sin s\;ds\;dr\;d\phi$$

of particles, which proceed in unit time with speed $\omega$ from the volume-element $r^2\,dr\sin s\,ds\,d\phi$ expressed in polar coordinates with $dS$ as origin and the normal to $dS$ as axis. $N$, $m$, and $\mathrm{B}$ are here magnitudes which have different values for the two kinds of gas, and must therefore be distinguished by subscripts 1 and 2. $N$ and $\mathrm{B}$ are also functions of the position; but it will be sufficient in the case of $\mathrm{B}$, the collision-frequency, to assume a mean constant value, and consequently to take into account only with respect to $N$ that we must employ that value of it which is proper for the position of the volume-element $r^2dr\sin s\,ds\,d\phi$, and which should be indicated by the argument $x - r\cos s$. Since $r$ is small, the function $N$ with this argument may be put

$$N(x - r\cos s) = N - \frac{dN}{dx}r\cos s,$$

where the letter $N$ without any argument denotes the value at the position $x$.

We are not concerned with the whole number of particles that pass through $dS$, but only with the difference between the numbers which pass from the right and from the left; this difference does not depend on the absolute value of $N$, but is conditioned only by its variation. Hence, on introducing into the above formula the expression we have developed for $N$, we neglect the first term and investigate only the second

$$-\frac{dN}{dx}(km/\pi)^{\frac{3}{2}}\mathrm{B}e^{-\mathrm{B}r/\omega}e^{-km\omega^2}\omega^2d\omega\;dS\cos^2 s\sin s\;ds\;rdr\;d\phi,$$

which we have to integrate between 0 and $\infty$ in respect to $\omega$ and $r$, over unit area as regards $dS$, from 0 to $\frac{1}{2}\pi$ in respect to $s$, and from 0 to $2\pi$ in respect to $\phi$. We thus obtain as expression for the number which pass through unit area in the direction of increasing $x$, in consequence of the unequal distribution,

$$-\frac{2}{3\sqrt{\pi}}\frac{dN}{dx}(km)^{\frac{3}{2}}\int_0^\infty d\omega\;\omega^4\mathrm{B}^{-1}e^{-km\omega^2}.$$

For the number passing in the opposite direction the same expression holds, but with changed sign.

## 52*. Signification and Value of the Integral

The integral that occurs in the last formula has a simple meaning, in virtue of which we are enabled to solve the problem in § 95, viz. to find the mean perpendicular distance, represented by $\Delta$, by which the original layers of the molecules that diffuse through any section are distant from that section.

In the preceding paragraph we first found the number of the particles meeting the section considered; to this was added the factor $r \cos s$, or the perpendicular distance of one of the original layers, by the development of the function $N$. Consequently the somewhat altered expression

$$\tfrac{2}{3}\pi^{-\frac{1}{2}}N(km)^{\frac{3}{2}}\int_0^\infty d\omega\, \omega^4 \mathrm{B}^{-1}e^{-km\omega^2}$$

would be nothing else than the sum of the perpendicular distances for all the particles that meet the unit area in unit time. If we divide this sum by the number of particles that meet the area, which by § 41* is $\frac{1}{4}N\Omega$, we obtain the mean value we are seeking,

$$\Delta = \tfrac{8}{3}\pi^{-\frac{1}{2}}\Omega^{-1}(km)^{\frac{3}{2}}\int_0^\infty d\omega\, \omega^4 \mathrm{B}^{-1}e^{-km\omega^2}.$$

Employing as before the symbol $M$ to denote the mean value of a magnitude within brackets, as calculated on the assumption of Maxwell's law, we may write for this

$$\Delta = \tfrac{2}{3}\Omega^{-1}M(\omega^2/\mathrm{B}) = \tfrac{2}{3}\Omega^{-1}M(\omega l),$$

where $l$ is the mean free path of the molecules moving with the speed $\omega$.

Since the integration cannot be carried out, we are obliged to estimate its value by approximations. It seems sufficient to put for B its mean value, which was represented by $\Gamma$ in § 29*. We then get

$$\Delta = \tfrac{2}{3}\Omega^{-1}\Gamma^{-1}M(\omega^2),$$

and hence, since by § 19* the mean value of $\omega^2$ is

$$M(\omega^2) = G^2 = \tfrac{3}{8}\pi\Omega^2,$$

we obtain

$$\Delta = \tfrac{1}{4}\pi\Omega/\Gamma = \tfrac{1}{4}\pi\mathfrak{L},$$

where $\mathfrak{L}$ is the mean free path of the molecules.

## 53*. Coefficient of Diffusion

This result enables us also to express in terms of the free path the number of molecules, represented by the last formula in § 51*, which pass over unit area in unit time in the direction of increasing $x$: for this we have

$$-\tfrac{1}{16}\pi\Omega\,\mathfrak{L}(dN/dx).$$

In the opposite direction flows an equal number with changed sign, so that

$$-\tfrac{1}{8}\pi\Omega\,\mathfrak{L}(dN/dx)$$

more particles cross in the positive direction than in the negative.

If now we introduce the necessary subscripts for the two gases,

$$-\tfrac{1}{8}\pi\Omega_1\mathfrak{L}_1(dN_1/dx)$$

particles of the first kind and

$$-\tfrac{1}{8}\pi\Omega_2\mathfrak{L}_2(dN_2/dx)$$

particles of the second kind pass through unit area in unit time in the positive direction. By repeating the procedure employed in § 95, and remembering that

$$N_1 + N_2 \equiv N$$

is a constant independent of $x$, we obtain for the constant of diffusion the expression

$$D = \frac{\pi}{8N}(N_1\mathfrak{L}_2\Omega_2 + N_2\mathfrak{L}_1\Omega_1),$$

which agrees with the former one. We have to substitute in this the values of the free paths as in § 98; and we then obtain

$$D = \frac{\pi}{8N}(N_2\Omega_1{}^2\Gamma_1{}^{-1} + N_1\Omega_2{}^2\Gamma_2{}^{-1}),$$

where for shortness are put

$$\Gamma_1 \equiv \pi s_1{}^2N_1\Omega_1\sqrt{2} + \pi\sigma^2N_2\sqrt{(\Omega_1{}^2 + \Omega_2{}^2)}$$

$$\Gamma_2 \equiv \pi s_2{}^2N_2\Omega_2\sqrt{2} + \pi\sigma^2N_1\sqrt{(\Omega_1{}^2 + \Omega_2{}^2)}.$$

## 54*. Differential Equations

If this value of $D$ were constant, the differential equations

$$\frac{dN_1}{dt} = D\frac{d^2N_1}{dx^2},\quad \frac{dN_2}{dt} = D\frac{d^2N_2}{dx^2}$$

would hold good, if the composition of the mixture determined by $N_1$ and $N_2$ depends only on a single coordinate $x$ in addition to the time $t$. In that case $N_1$ and $N_2$ may be replaced by the partial pressures $p_1$ and $p_2$, which each gas would exert were it alone.

But if the coefficient of diffusion $D$ varies with $N_1$ and $N_2$, and consequently with $x$, the equations become

$$\frac{dN_1}{dt} = \frac{d}{dx}\left(D\frac{dN_1}{dx}\right) = D\frac{d^2N_1}{dx^2} + \frac{dD}{dx}\frac{dN_1}{dx}$$

$$\frac{dN_2}{dt} = \frac{d}{dx}\left(D\frac{dN_2}{dx}\right) = D\frac{d^2N_2}{dx^2} + \frac{dD}{dx}\frac{dN_2}{dx}.$$

But now

$$\frac{dD}{dx} = \frac{dD}{dN_1}\frac{dN_1}{dx} + \frac{dD}{dN_2}\frac{dN_2}{dx},$$

or, since the numbers $N_1$ and $N_2$ are connected by the equation

$$N_1 + N_2 = N,$$

in which $N$ denotes the whole number, independent of $x$ and $t$, of the particles in unit volume,

$$\frac{dD}{dx} = \left(\frac{dD}{dN_1} - \frac{dD}{dN_2}\right)\frac{dN_1}{dx} = \left(\frac{dD}{dN_2} - \frac{dD}{dN_1}\right)\frac{dN_2}{dx}.$$

The differential equations therefore take the form

$$\frac{dN_1}{dt} = D\frac{d^2N_1}{dx^2} + \left(\frac{dD}{dN_1} - \frac{dD}{dN_2}\right)\left(\frac{dN_1}{dx}\right)^2$$

$$\frac{dN_2}{dt} = D\frac{d^2N_2}{dx^2} + \left(\frac{dD}{dN_2} - \frac{dD}{dN_1}\right)\left(\frac{dN_2}{dx}\right)^2,$$

in which the square of the first differential coefficient with respect to the coordinate is involved as well as the second.

If the diffusion tube is long enough for the rate of change of the partial pressure of a gas to be very small, then $(dN_1/dx)^2$ and $(dN_2/dx)^2$ are small magnitudes which may be neglected. The equations then retake the simpler form

$$\frac{dN_1}{dt} = D\frac{d^2N_1}{dx^2}, \quad \frac{dN_2}{dt} = D\frac{d^2N_2}{dx^2},$$

but they contain a factor $D$ which depends on $N_1$ and $N_2$, and thus varies with $x$ and $t$. If we are to assume solutions of these equations of the usual form, we shall have so to arrange our experiments that $N_1$ and $N_2$, and therefore also $p_1$ and $p_2$, may alter with time and place in only a very slight degree.

# APPENDIX VI

## *CONDUCTION OF HEAT*

### 55*. Transference of Energy

As interpreted in our theory, viscosity and heat-conduction are closely allied phenomena. Viscosity consists in the transference of the forward momentum of the molecules from layer to layer; heat-conduction is the transference of the kinetic energy of the molecular motions from place to place.

The calculation of the heat-conduction is thus to be begun and carried out quite analogously to that of viscosity in § 47*. The only difference consists in this: that in place of the $y$-directed momentum $m\omega \sin s \cos \phi$, is to be substituted the total kinetic energy, which is $\frac{1}{2}m\omega^2$ if we here neglect atomic motions and consider those of the molecules only. If, then, we assume the gaseous medium to be practically at rest so far as the exterior is concerned, we obtain the formula

$$Q = \tfrac{1}{2}m\int_0^{2\pi} d\phi \int_0^{\frac{1}{2}\pi} ds \sin s \cos s \int_0^{\infty} dr N(km/\pi)^{\frac{3}{2}} \int_0^{\infty} d\omega\ \omega^4 \mathrm{B} e^{-\mathrm{B}r/\omega} e^{-km\omega^2},$$

which denotes the kinetic energy or heat carried across unit area of a surface in unit time in the direction of increasing $x$.

Maxwell's law, which the formula assumes, is of course strictly applicable only to the case of a gas in a perfectly uniform state throughout, and not for one in which the mass and motion are unequally distributed. But, just as for viscosity and diffusion, the application of Maxwell's law to the case of heat-conduction also is justifiable as a sufficient approximation to the truth, if only the change in the values of the variable magnitudes with place occurs everywhere sufficiently slowly, so that a constant state may be assumed to exist in a tolerably large region.

For the problem of heat-conduction the most important of the magnitudes which vary with place is the mean value of the molecular energy which, by a formula developed before in § 19*, p. 388, is determined by the magnitude $k$. Further, the number of molecules per unit volume $N$ must also vary from place to place, because the warmer parts of the gas are more expanded than the colder. And, finally, the magnitude B, or the collision-frequency, is also variable with the place.

As regards the last magnitude, I shall again neglect its variableness with place, as in our former investigations of viscosity and diffusion; for the approximation will be permissible that in the short length of a molecule's free path a constant mean value of B may be substituted for what is in reality a variable value.

The two other magnitudes $N$ and $k$ must, however, be both treated as variable. By reason of their continuity we can use Taylor's theorem to find from their values at a point $(x, y, z)$ their values at any neighbouring point. This last, referred to the former, we denote by the relative coordinates $r, s, \phi$. Since only very small values of the distance $r$ come into consideration, by reason of the smallness of the molecular free paths, we can limit the expansions by Taylor's theorem to the first two terms, more especially as the functions are, on our assumption, to vary only very slowly. Assuming therefore that the heat-condition of the medium varies only in the direction of the coordinate $x$, we may put

$$k \mp \frac{dk}{dx} r \cos s \quad \text{and} \quad N \mp \frac{dN}{dx} r \cos s$$

instead of $k$ and $N$, where both functions are to be taken with their values at the point $(x, y, z)$, and the upper or lower sign is to be taken according as the position $(r, s, \phi)$ lies nearer to or further from the origin of the $x$-coordinates than the point $(x, y, z)$.

If we further neglect the square of $r$, we then obtain for the kinetic energy which passes through unit area in unit time at the point $(x, y, z)$ in the direction of $x$ the amount

$$Q = \tfrac{1}{2} Nm(km/\pi)^{\frac{3}{2}} \int_0^{2\pi} d\phi \int_0^{\frac{1}{2}\pi} ds \sin s \cos s \int_0^{\infty} dr \int_0^{\infty} d\omega\, \Psi,$$

wherein $N$ and $k$ have the meanings last defined, and $\Psi$ is given by

$$\Psi \equiv \omega^4 \mathrm{B} e^{-\mathrm{B}r/\omega} e^{-km\omega^2} \left[ 1 \mp \left\{ \frac{1}{N}\frac{dN}{dx} + (\tfrac{3}{2}k^{-1} - m\omega^2)\frac{dk}{dx} \right\} r \cos s \right],$$

the upper sign corresponding to a flow in the direction of increasing $x$, and the lower to one in the direction of decreasing $x$.

## 56*. Conditions for the Stationary State

Since the two magnitudes $N$ and $k$ are simultaneously variable together, either can be considered as a function of the other. For the complete solution of this problem the determination of their mutual relation is necessary. This can, as Clausius[1] has taught, be obtained from the condition that the transfer of heat is not bound up with a simultaneous transfer of mass.

If we make the further assumption that the state of flow of heat has become stationary, the following three propositions hold, according to Clausius:

(1) The *mass* of gas which passes in unit time through the $yz$-surface in the direction of increasing $x$ must be equal to that which passes through it in the reverse direction, *i.e.* of decreasing $x$; for otherwise the density would alter with the time.

(2) The *momentum* which passes in the positive direction in excess of that which passes in the negative direction must have the same value for every section, and thus be independent of $x$. For if through two parallel planes there did not pass equal quantities, on the one hand, into the space lying between the planes, and, on the other, out of this same region, the mass in it would increase in momentum and so in speed.

(3) The *energy* which passes through any section must, just as the momentum, exhibit at every position of the section, *i.e.* for every value of $x$, the same excess of quantity crossing in the direction of increasing $x$ over that crossing in the opposite direction.

These three propositions may be expressed in the form of equations, each of which contains an integral of the form of that just given. The three integrals differ in that for the first the factor $\frac{1}{2}m\omega^2$ is absent; for the second it is replaced by $m\omega \cos s$; and for the third it remains as it is.

We satisfy Clausius' second and third propositions, at least with sufficient approximation, by the assumption that $N$ and $k$ are linear functions of $x$. For then the differential coefficients are constant, and as, according to the hypothesis of slow variation assumed before, these are small in value, and are, moreover, multiplied by the small quantity $r$, the variations of $N$ and $k$ may be neglected in their coefficients.

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[1] 'Ueber die Wärmeleitung gasförmiger Körper,' § 16, *Pogg. Ann.* 1862, cxv. p. 32; *Abhandlungen über Wärmetheorie*, 2. Abth. p. 303, 1867.

But we can satisfy the first proposition, viz. that the transference of heat is not carried out by a transport of heated masses, only by the assumption of some relation between $N$, B, and $k$. After carrying out some easy integrations, we obtain the equation

$$0=\int_0^\infty d\omega\,\omega^4 \mathrm{B}^{-1} e^{-km\omega^2}\left\{\frac{1}{N}\frac{dN}{dx}+\left(\tfrac{3}{2}k^{-1}-m\omega^2\right)\frac{dk}{dx}\right\}.$$

For the performance of this integration there are two methods of approximation, which have been already employed in the theory of viscosity, of which the one consists in our putting the constant mean value of B, the collision-frequency, in the place of B, while in the second we substitute the mean value of the free path $l \equiv \omega/\mathrm{B}$ instead of its actual value. The former method gives for the integral a value too large; the second, one too small. By both we arrive at a relation between the differential coefficients which is of the form

$$0=\frac{1}{N}\frac{dN}{dx}-\frac{h}{k}\frac{dk}{dx}:$$

here $h=1$ according to the former method, and according to the latter $h=\frac{1}{2}$.

The true value of $h$ must lie between these. It would then be practically sufficient if, without seeking to exactly evaluate the integral, we assumed the mean value $h=\frac{3}{4}$, and eliminated the differential coefficient of $N$ from $\Psi$ by means of the equation

$$\frac{1}{N}\frac{dN}{dx}=\frac{3}{4k}\frac{dk}{dx}.$$

We should obtain

$$\Psi=\omega^4 \mathrm{B} e^{-\mathrm{B}r/\omega} e^{-km\omega^2}\left\{1\mp\left(\tfrac{9}{4}k^{-1}-m\omega^2\right)\frac{dk}{dx}\,r\cos s\right\}.$$

But it is also possible to calculate the value of $h$ with exactness, if we are not afraid of the tedious work of calculating by a mechanical quadrature the values of both terms of the integral which is above put equal to zero, just as, indeed, the similar integral in § 48* occurring in the theory of viscosity was treated. This calculation, too, has been made by W. Conrau, who has communicated to me his result, viz.:

$$h=0{\cdot}71066,$$

which gives for $\Psi$ the value

$$\Psi=\omega^4 \mathrm{B} e^{-\mathrm{B}r/\omega} e^{-km\omega^2}\left\{1\mp\left(2{\cdot}21066\,k^{-1}-m\omega^2\right)\frac{dk}{dx}\,r\cos s\right\}.$$

## 57*. Conductivity

The integration, so far as it can be carried out, gives that the energy which crosses unit area in unit time in the direction of increasing $x$ has the value

$$Q=\frac{N}{4\sqrt{(\pi k^3 m)}}-\tfrac{1}{3}\pi Nm\frac{dk}{du}(km/\pi)^{\frac{3}{2}}\int_0^\infty d\omega\,\omega^6\mathrm{B}^{-1}(2{\cdot}2107\,k^{-1}-m\omega^2)e^{-km\omega^2}.$$

The first of these terms, which is constant, may be put into the more intelligible form

$$\tfrac{1}{32}\pi mN\Omega^3.$$

In the opposite direction, that of decreasing $x$, there passes a quantity of kinetic energy, the expression for which differs from that just given only by the sign of the second term. The flow of heat in the positive direction resulting from both transfers, which, in accordance with Fourier's theory, is put proportional to the conductivity $\mathfrak{k}$ and to the differential coefficient of the temperature $\vartheta$ with negative sign, is the difference between the two magnitudes, or

$$-\mathfrak{k}\frac{d\vartheta}{dx}=-\tfrac{2}{3}\pi mN(km/\pi)^{\frac{3}{2}}\frac{dk}{dx}\int_0^\infty d\omega\,\omega^6\mathrm{B}^{-1}(2{\cdot}2107\,k^{-1}-m\omega^2)e^{-km\omega^2}.$$

Now, as we found before in § 19*, p. 388,

$$km=4\pi^{-1}\Omega^{-2}=4\pi^{-1}\Omega_0^{-2}/(1+\alpha\vartheta),$$

where $\Omega_0$ is the mean molecular speed at the temperature $\vartheta=0°$ C. and $\alpha$ is the coefficient of expansion; consequently

$$m\frac{dk}{dx}=-4\pi^{-1}\Omega_0^{-2}\alpha(1+\alpha\vartheta)^{-2}\frac{d\vartheta}{dx}=\frac{\alpha km}{1+\alpha\vartheta}\frac{d\vartheta}{dx}.$$

We therefore obtain for the conductivity

$$\mathfrak{k}=\tfrac{2}{3}\pi^{-\frac{1}{2}}N(km)^{\frac{5}{2}}\alpha(1+\alpha\vartheta)^{-1}\int_0^\infty d\omega\,\omega^6\,\mathrm{B}^{-1}(m\omega^2-2{\cdot}2107\,k^{-1})e^{-km\omega^2}.$$

To reduce this expression to thermal units—for energy is expressed in it in mechanical units—we note that the kinetic energy of unit mass is

$$\tfrac{1}{2}\cdot\tfrac{3}{8}\pi\Omega^2=\tfrac{3}{4}(km)^{-1},$$

while on the other hand the heat at temperature $\vartheta°$ C. (or absolute temperature $\vartheta+\alpha^{-1}$), which is equivalent to it, is

$$c(\vartheta+\alpha^{-1}),$$

where $c$ denotes the specific heat at constant volume. Hence the conductivity expressed in thermal units is

$$\mathfrak{k} = \tfrac{8}{9}\pi^{-\frac{1}{2}}Nc(km)^{\frac{7}{2}}\int_0^\infty d\omega\, \omega^6 \mathrm{B}^{-1}(m\omega^2 - 2{\cdot}2107\ k^{-1})e^{-km\omega^2}$$

$$= \tfrac{8}{9}\pi^{-\frac{1}{2}}Nc(km)^{\frac{7}{2}}\int_0^\infty d\omega\, \omega^5 l(m\omega^2 - 2{\cdot}2107\ k^{-1})e^{-km\omega^2},$$

where $l$ is the mean free path of the particles which move with speed $\omega$.

We find upper and lower limits of the value of this integral by the approximate methods employed in former paragraphs, in which we put for B or $l$ their mean values. In this calculation I have not taken the exact value of $h$, but its approximate value $\frac{3}{4}$, and therefore 2·25 instead of 2·2107; and I have obtained

$$\tfrac{1}{3}mN\Omega Lc < \mathfrak{k} < \tfrac{25}{96}\pi mN\Omega Lc,$$

or

$$0{\cdot}333\ mN\Omega Lc < \mathfrak{k} < 0{\cdot}818\ mN\Omega Lc.$$

If we compare this determination with the theoretical value of the coefficient of viscosity, which with sufficient approximation is given by

$$\eta = \pi^{-1}mN\Omega L,$$

we have

$$\tfrac{1}{3}\pi\eta c < \mathfrak{k} < \tfrac{25}{96}\pi^2\eta c,$$

or

$$1{\cdot}047\ \eta c < \mathfrak{k} < 2{\cdot}570\ \eta c,$$

so that the upper limit coincides nearly exactly with that calculated by Boltzmann.

Since these limiting values are rather far apart, an exact evaluation of the integral by mechanical quadrature, as in the case of viscosity, is necessary. This has been very kindly done at my request by P. Neugebauer, by means of the tables left behind by Conrau; and my best thanks are due to him for his kindness. The calculation has given that, if $h$ is taken equal to $\frac{3}{4}$,

$$\mathfrak{k} = 1{\cdot}53716\ \eta c,$$

as was assumed in the first edition of this book; but with the more correct value 0·71066 for $h$ calculated by Conrau we have

$$\mathfrak{k} = 1{\cdot}6027\ \eta c.$$

This value lies between those calculated by Clausius and Maxwell, viz. $\frac{5}{4}\eta c$ and $\frac{5}{3}\eta c$ respectively. A comparison of these theoretical formulæ with experiment is given in § 108.

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